Sixth Annual Report

on

MATERIALS RESEARCH AT STANFORD UNIVERSITY

July 1, 1966, to June 30, 1967

CENTER FOR MATERIALS RESEARCH

STANFORD UNIVERSITY • STANFORD, CALIFORNIA

Sixth Annual Report

on

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Information concerning research activities related to the science of materials during the period July 1, 1966 to June 30, 1967.

This research was supported by one or more of the following agencies of the United States Government:

Advanced Research Projects Agency of the Department of Defense
Atomic Energy Commission
Department of the Air Force
Department of the Army
Department of the Navy
National Aeronautics and Space Administration
National Institutes of Health
National Science Foundation

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to the
ADVANCED RESEARCH PROJECTS AGENCY

by the
CENTER FOR MATERIALS RESEARCH
STANFORD UNIVERSITY
STANFORD, CALIFORNIA

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SECTION A

INTRODUCTION

This Sixth Annual Report includes information briefly describing the total research activity related to the science of materials at Stanford University during the period July 1, 1966, through June 30, 1967.

The research described herein received financial support from many different sources. As indicated in their descriptions, most of the specific research programs were directly supported by one or more of the following agencies of the United States Government.

Advanced Research Projects Agency of the Department of Defense
Atomic Energy Commission
Department of the Air Force
Department of the Army
Department of the Navy
National Aeronautics and Space Administration
National Institutes of Health
National Science Foundation

In addition to the direct support of individual research programs by the agencies mentioned above, overall assistance and broad-base support was furnished by the Advanced Research Projects Agency to materials research activities at Stanford through its Materials Sciences Interdisciplinary Laboratory Program under Contract SD-87, which is administered by the Center for Materials Research.

This report contains brief descriptions of the various individual research programs active during the period July, 1966, through June, 1967, arranged alphabetically by the name of the principal investigator. Also included are lists of publications, doctoral dissertations, faculty and senior staff members, research associates, graduate students and degrees awarded. Finally, a name index is included for convenience in locating references to the activities of specific individuals.

From this compilation it can be seen that research on materials and related problems is being conducted within twelve different academic departments or divisions at Stanford. Work on materials engineering, materials applications, and other peripheral areas is also being undertaken in these, as well as in other, departments. Such work is not included in this compilation, however.

SECTION B

MATERIALS RESEARCH PROGRAMS

1. RHEOLOGICAL PROPERTIES OF VISCOELASTIC MATERIALS

A. Acrivos, Professor, Chemical Engineering
W. H. Schwarz, Professor Chemical Engineering

Graduate Students:

C. A. Bruce
N. A. Frankel

Agency Support:

NSF GK 1245

Research Report:

(1) Viscometric Study of Viscoelastic Materials

Graduate Student: C. A. Bruce

A Weissenberg rheogoniometer was recently acquired for the purpose of determining experimentally the viscometric properties of viscoelastic materials such as dilute solutions of long-chain organic macromolecules. This instrument can be used for steady shearing, for periodic shearing or for both, and involves three separate attachments: 1) a cone and plate; 2) two parallel plates; and, 3) two co-axial cylinders.

In steady motion experiments, the cone and plate was found best for determining shear stresses, whereas, for normal stress measurements, both the cone and plate and the parallel plates had to be used. In addition, complex viscosities were measured in an oscillatory motion using the parallel plates and the co-axial cylinders.

At present, an attempt is being made to increase the range of the viscometer into the region of very low rates of strain.

2. INTERACTION OF ACOUSTIC AND ELECTROMAGNETIC RADIATIONS IN SOLIDS

B. A. Auld, Research Physicist, Hansen Laboratory
M. Chodorow, Professor, Applied Physics and Electrical Engineering

Professional Associate:

J. H. Collins (Visiting)

Graduate Students:

R. C. Addison
S. I. Wax
D. C. Webb
J. H. Wilkinson
D. A. Wilson
D. C. Wolkerstorfer
H. R. Zapp

Agency Support:

ONR N00014(67)A-0112-0001
ONR Nonr 225(48)
AF 19(628)-5545
AF 30(602)-3595

Research Report:

(1) Doppler Shift and Adiabatic Conversion Methods in Solids

Graduate Student: R. Zapp

This is a theoretical and experimental study to examine the possibility of producing a useful frequency conversion and/or amplification by means of moving interfaces between regions having different wave propagation characteristics. Some experiments have been performed on the Doppler shift of light scattered from traveling and standing acoustic waves in transparent solids. Theoretical studies of reflection and transmission at a moving abrupt interface or series of interfaces have been extended by treating the case of a tapered transition. This has been treated by both the Lorentz transformation method and an energy balance method. On the basis of this theory a method has been devised for adiabatically converting a transverse acoustic wave into an amplified longitudinal wave at approximately twice the frequency, using ferrimagnetic materials.

By applying ray theory to the problem it has been found that the magnetoelastic beam in a delay line is strongly focused and has a diameter less than 100μ at the end face of the sample. Another outcome of these ray path studies has been to demonstrate the inadequacy of the conventional theory of delay line excitation. A more satisfactory theory has been developed in a qualitative fashion by using ray theory concepts. According to this theory excitation of a magnetostatic wave occurs at the end face of the sample. These propagate into the sample and reflect into magnetoelastic waves at the turning surface. An attempt will be made to reach a satisfactory compromise by using periodic focusing structures.

(3) Delay Line Studies

Graduate Student: D. C. Webb

The conventional magnetoacoustic delay line utilizes a single crystal YIG rod in an axial magnetic field. This structure has a single, common input and output port, and is therefore unsatisfactory for some applications. Various proposals have been made for magnetoacoustic delay lines having two accessible ports. The subject of this project is the YIG-YAG-YIG structure, a two-port structure which is found to have advantages for pulse compression applications. A model of this device has been constructed and tested. Insertion loss of 47 dB at 4.7 μsec delay was measured at 950 mc/sec; and variable delay from 3 to 8 μsec was obtained. These experiments also provided experimental confirmation of the excitation mechanism studied under (2).

(4) Infrared Bragg Scattering from Coherent Spin Waves of Magnetoacoustic Waves

Graduate Student: D. A. Wilson

Theoretical work has been done on new interactions between optical waves, acoustic waves, and spin waves in ferrites. Because of the infrared transmission window in YIG it is possible to consider interactions of infrared waves with acoustic waves and spin waves in this material. This proposed scattering could provide a useful tool

forces on the electron spins produced by the nonuniform magnetic field of the spin wave. The problem is treated by considering separately the positive and negatively polarized electrons and applying space charge wave analysis to find the normal modes. These modes are coupled to the spin wave modes and the equations solved for the growth rate. For a 1000 volt 10 mA beam and a spin wave number of 10^5 the growth factor is only 1 cm^{-1}, which does not permit net gain with currently available spin wave line widths.

Reference Publications and Presentations:

1. C. S. Tsai and B. A. Auld, "Wave Interactions with Moving Boundaries: Part I, Single Boundary; Part II, Multiple Boundaries," J. Appl. Phys. 38 (5) 2106-2115 (Apr. 1967).

2. C. S. Tsai and B. A. Auld, "Multiple Acoustic Diffraction Techniques for Frequency Shifting of Laser Sources," Proc. IEEE 54 (9) 1217-1218 (Sept. 1966).

3. R. C. Addison, B. A. Auld, and J. H. Wilkinson, "Electrically Controlled Acoustic Beam Deflection," Proc. IEEE 55, 68-77 (Jan. 1967).

4. R. C. Addison, B. A. Auld, and J. H. Collins, "Ray Path Trajectories in Magnetic Delay Lines," Presented at 12th Conference on Magnetism and Magnetic Materials, Washington, D. C. (Nov. 1966).

5. B. A. Auld and D. A. Wilson, "Bragg Scattering of Infrared Radiation from Coherent Spin Waves," Microwave Laboratory Report No. 1472, Stanford University (Sept. 1966); submitted to J. Appl. Phys.

6. B. A. Auld, J. H. Collins, and H. R. Zapp, "Spinwave-Frequency Conversion by Adiabatic Field Pulsing," Electronics Letters 3 (1) (Jan. 1967).

7. J. H. Collins, "Simultaneous Propagation of Magnetostatic and Spin-Elastic Waves in Nonellipsoidal Ferrimagnets," Electronics Letters 3 (2) (Feb. 1967).

8. B. A. Auld, C. F. Quate, H. J. Shaw, and D. K. Winslow, "Acoustic Quarter-Wave Plates at Microwave Frequencies," Appl. Phys. Letters 9 (12) 436-438 (Dec. 1966).

3. NUCLEAR MAGNETIC RESONANCE AND ION CYCLOTRON RESONANCE SPECTROSCOPY

J. D. Baldeschwieler, Professor Chemistry

Professional Associates:

L. R. Anders
H. Shimizu

Graduate Students:

J. L. Beauchamp
L. K. Blair
T. T. Bopp
R. G. Bryant
S. E. Buttrill, Jr.
R. C. Dunbar
W. T. Huntress, Jr.
A. G. Marshall
R. E. Moll
P. G. Schmidt
B. D. Sykes
D. Wallach

Agency Support:

NSF GP 4924-x
USPHS GM 14752-01
ARPA SD-87

Technical Objectives:

The objectives of this work are to develop techniques for the study of molecular diffusion and macromolecular structure by nuclear magnetic resonance, and to develop techniques for the study of ion-molecule reactions by cyclotron resonance spectroscopy.

Research Report:

(1) The Measurement of Translational Diffusion Coefficients in Liquids and Solids by Pulsed NMR Techniques

Graduate Students. R. E. Moll
B. D. Sykes

The spin-echo NMR technique developed for the study of translational diffusion of macromolecules has been applied to measure the

(3) Halide Ions as Chemical Probes for NMR Studies of Macromolecules

Graduate Students: R. G. Bryant
A. G. Marshall

The binding and exchange of halide ions with specific sites in macromolecules provides a surprisingly high gain chemical amplifier which allows the NMR study of macromolecules in solution at concentrations below 10^{-6} molar. The technique has been applied to help map the active site of α-chymotripsin.

(4) The Study of Protein-Substrate Interactions by Proton-NMR Spectroscopy

Graduate Student: P. G. Schmidt

NMR spectroscopy has been applied to the direct study of the proton spectra of ribonuclease and lysosyme in solution. It is possible to obtain structural information on these macromolecules with instrumentation operating at 100 megacycles using multiple scan techniques. Changes in the linewidth and chemical shifts of the proton resonances of various substrates and inhibitors are also indicative of the details of their interactions with proteins. This technique has been used to probe allosteric effects in hemoglobin and aspartic transcarbamolase.

(5) The Study of Ion-Molecule Reactions by Cyclotron Resonance Spectroscopy

Graduate Students: J. L. Beauchamp
L. K. Blair
S. E. Buttrill, Jr.
R. C. Dunbar

Ion cyclotron resonance, and ion cyclotron double resonance spectroscopy have been applied to the study of ion-molecule reactions in the gas phase. The technique has been applied to a variety of simple systems to develop the systematic chemistry of ion-molecule reactions. Some of these systems include the chemistry of the alkyl halides, simple aliphatic and heterocyclic alcohols and ethers, aromatic hydrocarbons, and the boron hydrides. It is apparent that ion cyclotron resonance spectroscopy is a very powerful technique for determining

11. B. D. Nageswara Rao and L. Lessinger, "Effect of Relaxation on the Nuclear Double Resonance Spectra of Weakly Coupled Spin Systems; Proton Double Resonance in Ethyl Fluoride," Mol. Phys, 12, 221 (1967).

12. W. T. Huntress, Jr., "The Effects of Anisotropic Molecular Rotational Diffusion on Nuclear Magnetic Relaxation in Liquids," in press.

13. A. G. Marshall, "Nuclear Magnetic Resonance Study of α-Chymotrypsin," in press.

14. T. T. Bopp, "Magnetic Resonance Studies of Anisotropic Molecular Rotation in Liquid Acetonitrile -d_3," in press.

15. D. Wallach, "Effect of Internal Rotation on Angular Correlation Functions," in press.

16. J. D. Baldeschwieler, "Ion Cyclotron Resonance Spectroscopy," Science, in press.

17. R. C. Dunbar, "Energy-Dependence of Ion-Molecule Reactions," J. Chem. Phys. (note), in press.

18. J. L. Beauchamp and S. E. Buttrill, Jr., "Proton Affinities of H_2S and H_2O," J. Chem. Phys., in press.

Theses Completed During Report Period:

1. Yoko Kanazawa, "Nuclear Spin Relaxation in Difluoroethylenes," (Harvard, 1966).

2. Leslie R. Anders, "Nuclear Magnetic Resonance Studies and Study of Ionic Collision Processes by Ion Cyclotron Double Resonance Spectroscopy," (Harvard, 1966).

(2) Investigation of Deformation and Fracture Mechanisms in Brazed Joints

Graduate Student: H. J. Saxton

This research is concerned with the deformation and fracture mechanisms in thin, brazed joints. Fe-3%Si brazed with Ag is used as a model material. The deformation and fracture characteristics of this composite system are being studied in an effort to correlate the macroscopic behavior with observations of the microscopic deformation mechanisms as observed by dislocation etch pitting and transmission electron microscopy. The yield characteristics of the brazed joints are being studied as a function of braze geometry, cooling rate from braze temperature, and base metal yield strength.

(3) Study of Solute Distribution in Dilute Molybdenum Alloys

Graduate Student: R. J. Ryerson

Molybdenum alloys with small additions of Zr and/or Ti exhibit mechanical properties at elevated temperatures far superior to unalloyed molybdenum or to solid solution strengthened molybdenum. This increase in mechanical strength has been attributed to either the formation of a fine dispersion of zirconium or titanium carbide or to the existence of solute atom clustering (similar to G.P. zones). The present investigation is concerned with this problem and its objectives are to determine

(1) the distribution of residual interstitials in otherwise pure Mo;

(2) the distribution of Zr and/or Ti in otherwise pure Mo;

(3) the distribution of Zr and/or Ti in the presence of varying amounts of carbon.

The main experimental technique to be utilized will be field ion microscopy.

(4) High Temperature Deformation Kinetics

Graduate Students: T. V. Nordstrom
N. N. Singh-Deo
T. A. Taylor

5. PROPERTIES OF SURFACES AND CATALYSIS

M. Boudart, Professor, Chemical Engineering and Chemistry

Professional Associates.

J. E. Benson
R. Heckingbottom

Graduate Students:

A. W. Aldag
G. E. Bergstrom, III
W. N. Delgass
Y. Y. Huang
K. A. Klinedinst
D. A. Ollis
C. Parravano
L. D. Ptak
A. B. Walters

Agency Support:

AF 49(638)-1423,A-1
Am. Chem. Soc. - Pet. Res. Fund
Army DAHC04-67-C-0045
ARPA SD-87

Research Report:

(1) Dispersion of Metals

Graduate Students: A. W. Aldag
G. E. Bergstrom, III
L. D. Ptak

Platinum spherical particles with a mean diameter of 60 Å and a rather sharp size distribution have been stabilized by supporting them on a very pure graphitized carbon porous support. These particles do not sinter when heated from 500° to 900°C in vacuum. But treatment at this higher temperature changes by a factor of ten the selectivity of these platinum particles used as a catalyst for the isomerization of neopentane. This has been interpreted by an increase of (111) 'triplet' configurations at the surface of the fired metal. Because of its stability and resistance to sintering, the platinum-carbon sample

Some exploratory runs on a commercial iron catalyst and small particles of Fe_3O_4 on graphon gave interesting spectra. More pertinent to our current plans are the spectra taken on iron exchanged into Linde Synthetic Zeolite, Type Y. We have found that:

1) We can do the exchange and observe the Mössbauer spectrum of iron in zeolites.

2) Changes in treatment of the zeolite sample such as heating and evacuation cause changes in the Mössbauer spectrum of the iron.

The first result is crucial since it indicates that our experimental program in zeolites can proceed as planned. The second finding confirms the importance of water on the zeolite system and the possibility of elucidating its effects.

Further studies on the nature of the iron zeolites and their interaction with water and adsorbing gases are planned. A parallel program on the Surface Mössbauer Spectroscopy of catalysts and adsorbents containing tin is being initiated.

Reference Publications:

1. C. Parravano, J. D. Baldeschwieler, M. Boudart, "Diffusion of Water in Zeolites," Science 155 (3769)1535-1536 (Mar. 1967).

2. M. Boudart, A. Aldag, J. E. Benson, N. A. Dougharty, and C. G. Harkins, "On the Specific Activity of Platinum Catalysts," J. Catalysis 6 (1) 92-99 (Aug. 1966).

3. J. E. Benson and M. Boudart, "Reversible Adsorption of Hydrogen on Near-Faujasites," J. Catalysis 8 (1) 93-95 (May 1967).

Research Report:

(1) Photoelectronic Properties of ZnSe Crystals[1]

Graduate Student: G. B. Stringfellow

Imperfections responsible for optical absorption, red and green luminescence emission, and photoconductivity have been investigated in single crystals of ZnSe:Cu showing p-type dark conductivity corresponding to a Fermi level 0.69 eV above the valence band. Results may be conveniently summarized in terms of a multivalent copper impurity model involving $Cu^{'}$ and Cu^{x} centers responsible for the red and green luminescence emission bands respectively. The observed effects of variation in Fermi level position as the result of annealing in Zn or in Se, or by incorporation of donor or additional Cu impurities, confirm this model. The similarity between the behavior of Cu, Ag, and Au impurities in II-VI compounds suggests that a similar model may be applicable to Ag and Au as well. Some of the properties of self-activated ZnSe were also investigated.[2]

(2) Photoelectronic Properties of CdSe Crystals

Graduate Student: A. L. Robinson

Pure CdSe crystals were grown from the melt and were characterized by conductivity, Hall effect, and photoconductivity measurements. These crystals were then made insulating and photosensitive by (a) annealing under various pressures of Se, (b) annealing in an inert atmosphere or vacuum, (c) incorporation of Cu or Ag impurity. The photoelectronic properties of these various resultant crystals are being investigated and compared.

(3) Electron Radiation Damage Effects in II-VI Compounds

Graduate Student: H. B. Im

The effects of electron radiation damage at room temperature were investigated in crystals of CdS as a function of electron energy and dosage, using photoelectronic techniques. It was found that electrons with energy 400 KeV or greater cause a large decrease in

(6) Photoconductivity Decay in Imperfect Crystals

By a comparison of theoretical decay curves calculated from the assumption of a quasi-continuous exponential trap distribution in imperfect crystals with experimentally measured decay curves in CdSSe sintered layer photoconductors as a function of temperature and excitation intensity, it is concluded that the decay can be described by specifying the electron lifetime and two trap distribution parameters.[7]

(7) Optical Quenching of Photoconductivity in CdS and ZnS Crystals

The optical quenching spectrum in CdS and ZnS single crystals was investigated as a function of temperature, using a high-resolution monochromator and polarized light. Poorly resolved fine structure was detected in the 0.9 eV quenching band in CdS between 0.83 and 0.92 eV, but no evidence of polarization effects. Studies of the temperature dependence of optical quenching confirm earlier indications of the intrinsically complex nature of sensitizing centers.[8]

(8) Photothermoelectric Effects in CdS

The use of the photothermoelectric effect was investigated for photoelectronic analysis, particularly of two-carrier effects. The effect has the intrinsic advantage over the Hall effect of having two-carrier behavior depend directly on the mobility ratio rather than on the ratio squared. Effects explored in this preliminary investigation were (a) variation of photothermoelectric effect with exciting wavelength, (b) optical quenching of the photothermoelectric effect, and (c) thermally stimulated thermoelectric effect.[9]

(9) Field Formulation of Rate Processes in Photoconductors

A conventional field approach, commonly used to describe the dynamic equilibrium of gases and sol d-state masers, is applied to

(13) Electro-optical Measurements on Impurity States in Crystals

Graduate Student: A. Jonath

Techniques of electroreflectance and electrotransmittance are being applied to gain information about the nature of the impurity states in crystals.

Reference Publications and Presentations:

1. G. B. Stringfellow, "Photoelectronic Properties of ZnSe Single Crystals," Ph.D. Thesis, Stanford University.

2. G. B. Stringfellow and R. H. Bube, "Photoelectronic Properties of p-Type ZnSe:Cu Crystals," Paper presented at the International Conference on II-VI Semiconducting Compounds, Brown University, Sept. 6-8, 1967, and published in the Proceedings of the Conference.

3. G. H. Blount, "Photoelectronic Properties of ZnS Single Crystals with Imperfections Induced by Annealing or Radioactive Impurities," Ph.D. Thesis, Stanford University (Mar. 1967).

4. G. H. Blount, A. C. Sanderson, and R. H. Bube, "Effects of Annealing on the Photoelectronic Properties of ZnS Crystals," J. Appl. Phys. 38 (11) 4409-4416 (Oct. 1967).

5. G. H. Blount, P. B. P. Phipps, and R. H. Bube, "Effects of Radioactive S^{35} in ZnS Crystals," J. Appl. Phys. 38 (11) 4550-4552 (Oct. 1967).

6. G. H. Blount, G. A. Marlor, and R. H. Bube, "Self-Diffusion of Sulfur in ZnS," J. Appl. Phys. 38 (9) 3795 (Aug. 1067).

7. R. H. Bube, W. M. Grove, R. K. Murchison, "Photoconductivity Decay in Imperfect Crystals," J. Appl. Phys. 38 (9), 3515-3518 (Aug. 1967).

8. S. O. Hemilä and R. H. Bube, "Optical Quenching of Photoconductivity in CdS and ZnS Crystals, paper presented at the March 1967 meeting of the American Physical Society, Chicago; submitted to J. Appl. Phys.

9. R. Lawrance and R. H. Bube, "Fine Structure in the Infrared Quenching Spectrum of CdS Single Crystals by Thermoelectric Studies," presented at the March 1967 meeting of the American Physical Society, Chicago.

7. EXPERIMENTS AT LIQUID HELIUM TEMPERATURES ON MACROSCOPIC QUANTUM EFFECTS, MATERIAL PROPERTIES AND GENERAL RELATIVITY

W. M. Fairbank, Professor, Physics
W. O. Hamilton, Assistant Professor, Physics
H. A. Schwettman, Associate Professor, Physics

Professional Associates:

I. L. Bass
E. E. Chambers
C. W. F. Everitt
L. V. Knight
M. S. McAshan
J. E. Opfer
T. I. Smith
V. S. Tuman
P. B. Wilson
F. C. Witteborn

Graduate Students:

T. D. Bracken
R. E. Brown
D. E. Claridge
H. D. Cohen
E. P. Day
D. B. Green
H. M. Griffiths
G. B. Hess
A. F. Hebard
L. B. Holdeman
J. Jehl
C. Lyneis
J. M. Madey
J. M. Pierce
P. B. Pipes
D. K. Rose
M. Taber
W. J. Trela
J. P. Turneure
J. P. Webb
E. Wilson

Agency Support:

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NASA NsG-582
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ONR Nonr 225(67)
AFOSR-68-1366
AF 33(615)67-C-1245
NSF GP 7416
ARPA SD-87

Technical Objectives:

There are several objectives to this research. One is to study the special quantum properties of He^3 and He^4. Another is to perform

(4) Quantized Vorticity in He^4 and its Effect as a Bubble Nucleation Center

Graduate Student: D. B. Greene

We are using a liquid He bubble chamber to examine the effects of vortex rings on bubble formation. We are using ultrasonic transducers to induce bubbles in the liquid and examining their formulation with photographs.

(5) Magnetic Properties of Cryogenic Construction Materials

Graduate Student: L. B. Holdeman

Using a sensitive superconducting magnetometer, we have measured the magnetic susceptibility of various construction materials, looking especially for permanent magnetism. Aluminum alloys are found generally to be nonmagnetic down to 2°K. Ti-6Al-4V alloy is also nonmagnetic down on 4°K.

(6) Magnetic Susceptibility of DNA

Graduate Student: J. M. Pierce and E. P. Day

We are developing an apparatus to look for changes in the magnetic susceptibility of DNA at the melting temperature. The apparatus uses a superconducting magnetometer while the sample is at room temperature. We are also building an apparatus to do magnetic resonance on samples with high water content. The use of superconducting circuits allows great sensitivity.

(7) Critical Point Phenomena

Graduate Students: H. M. Griffiths
J. P. Webb

We are studying the scattering of light from mixtures of He^3 and He^4 at the point of phase separation. We also are looking at light scattering from He^3 at the critical point. Preliminary data indicate that He^3 behaves like a Van der Waals gas at this point. Looking at

made a superconducting electron linear accelerator feasible and construction of such a device is now underway. Apparatus for further study of high frequency surface losses in superconductors near the transition temperature is being constructed.

(11) Force of Gravity on Elementary Charged Particles

Graduate Student: J. M. Madey

In attempting to measure the force of gravity on a free electron we discovered that the random electric fields outside a copper surface at low temperatures were much smaller than would be expected if the small crystals at the surface were randomly oriented and had their measured contact potentials. It may be that adsorbed gas on the surface is responsible for this dramatic reduction. We have also found a polarization of a metal in a gravitational field due to the force of gravity on the conduction electrons.

(12) Heat Transport by Superfluid Helium

Graduate Student: C. Lyneis

We are investigating the temperature drop along a rouge filled tube when heat is added at one end. The extremely high superfluid thermal conductivity makes possible large scale refrigeration at liquid helium temperatures. The large scale aspects will be tested in the superconducting accelerator.

(13) Josephson Tunneling and Weak Link Superconductors

Graduate Students: T. D. Bracken
D. E. Claridge

We are studying the mechanisms leading to the passage of magnetic flux through insulating and weak link junctions. The impedance the junctions offer is measured as the magnetic field on the junction is changed. We have built a very sensitive superheterodyne microwave system to detect these impedance changes. Measurements of this type will shed light on the quantum nature of the tunneling phenomena.

Reference Publications and Presentations:

1. W. M. Fairbank, W. O. Hamilton and C. W. F. Everitt, "From Quantized Flux to a Free Precession Nuclear Gyro," Proceedings of the OAR Research Applications Conference, Washington, D. C., 1966.

2. C. W. F. Everitt and W. M. Fairbank, "Application of Low Temperature Techniques in Satellite Experiment to Test General Relativity," Proceedings of X International Conference on Low Temperature Physics, Moscow, 1966.

3. W. M. Fairbank and W. O. Hamilton, "Quantized Flux, Zero Magnetic Field and Experiments on Time Reversal Invariance," ibid.

4. T. I. Smith, H. A. Schwettman, P. B. Wilson, and W. M. Fairbank, "Superconductivity and Particle Accelerators," ibid.

5. G. B. Hess and W. M. Fairbank, "Angular Momentum Defect in Rotating Helium II," ibid.

6. H. D. Cohen and W. M. Fairbank, "Nuclear Magnetic Susceptibility and Relaxation Times of a Dilute Solid Mixture of He^4 in He^3," ibid.

7. W. M. Fairbank, H. A. Schwettman, and T. I. Smith, "Superfluidity and Particle Accelerators," ibid.

8. W. M. Fairbank and A. L. Fetter, Chapter on Superconductivity, Condon's Handbook of Physics, 1967.

9. M. H. Edwards, R. M. Cleary, and W. M. Fairbank, "Bubble Formation on Vortices in a Liquid Helium Bubble Chamber," Proceedings of Symposium on Quantum Fluids, Sussex University, 1965 (North-Holland Publishing Co., Amsterdam, 1966).

10. P. B. Wilson, H. A. Schwettman, T. I. Smith, J. P. Turneaure, and W. M. Fairbank, "Applications of RF Superconductivity to Accelerators and Instrumentation," Proceedings of the International High Energy Instrumentation Conference, SLAC, Sept. 9-11, 1966.

11. T. I. Smith, H. A. Schwettman, W. M. Fairbank, and P. B. Wilson, "Stanford's Superconducting Accelerator Program," Proceedings of the 1966 Linear Accelerator Conference, Los Alamos, 491 (LA-3609).

8. MACROMOLECULAR RESEARCH

P. J. Flory, Jackson-Wood Professor, Chemistry

Professional Associates:

P. R. Schimmel
H. Hocker

Graduate Students:

B. E. Fichinger
S. Fisk
R. L. Jernigan
R. A. Orwoll
A. E. Tonelli
A. D. Williams

Agency Support:

AF 49 (638) 1341

Technical Objective:

To develop a better basis for understanding macromolecules and for interpreting their behavior.

Approach:

Currently, investigations are in two broad areas:

(1) the configurational statistics of long chain molecules, and the interpretation of such properties as spatial dimensions, dipole moments and optical anisotropies according to rigorous principles of statistical mechanics, and

(2) the thermodynamic properties of liquid solutions with major emphasis on solutions in which one component, at least, is macromolecular.

Progress:

See list of publications.

9. RESEARCH ON YIELDING OF METAL IN NOTCHES

H. O. Fuchs, Professor, Mechanical Engineering

Graduate Student:

T. L. Gerber

Agency Support:

ARPA SD-87

Technical Objective:

To define yield conditions in terms of stress gradients (or other appropriate parameters. Fatigue results lead us to believe that stress alone is not sufficient as a criterion.

Approach:

Statically load notched specimens with equal stress concentration factors but different stress gradients (or other appropriate parameters). Test for yield by checking fatigue strength which is very sensitive to the residual stresses which are produced by non-homogeneous yielding.

Research Report:

A first set of tests has been completed and a method of calculation has been worked out. Results to date indicate that prestressing can be very effective but requires loads much higher than those which would produce initial yielding if the full theoretical stress concentration were effective

Reference Publication and Presentation:

1. T. L. Gerber and H. O. Fuchs, "Analysis of Nonpropagating Fatigue Cracks in Notched Parts with Compressive Mean Stress," Presented at ASTM Annual Meeting, Boston, Mass., June 25-27, 1967.

and the reverse characteristics of pn diodes; measure transport properties of ions in insulating layers by using MOS capacitance-voltage measurements on insulating layers in which ions of desired type have been implanted; fabricate structures such as a Read diode where ion implantation offers a significant advantage over conventional doping techniques and study the properties of structures thus produced.

Research Report:

Equipment suitable for initial investigations has been constructed and successfully operated for the past 21 months. Since our last report we have

(1) Measured the profiles of B, P, Ni and As ions implanted at various energies into single crystal silicon targets.

(2) Developed a computer program for predicting the theoretical profiles based on available theories of particle stopping.

(3) Made fundamental contributions to stopping theory that explain the differences between experimental and theoretical implantation profiles.

(4) Made pn junctions in the II-VI compounds CdTe and began to investigate its properties.

(5) Made sulfur-doped ohmic contact in n-type GaAs for Gunn oscillators and other devices where normal ohmic contacts are inadequate.

(6) Obtained preliminary results on the energy levels and trapping constants of trapping centers introduced during ion implanation.

Reference Publications and Presentations:

1. W. S. Johnson and J. F. Gibbons, "Statistical Range Distribution of Ions in Single and Multiple Element Substrates," Appl. Phys. Letters 9 (9) 321-322 (Nov.1966).

2. W. S. Johnson, W. J. Kleinfelder, and J. F. Gibbons, "Projected Range Calculations from A Statistical Model," presented at IEEE 9th Annual Symposium on Electron, Ion and Laser Beam Technology, Berkeley, California, May 1967.

11. OPTICAL NETWORK SYNTHESIS USING BIREFRINGENT CRYSTALS

S. E. Harris, Assistant Professor, Electrical Engineering

Graduate Students:

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J. Falk
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Agency Support:

AFOSR F 19628-67-C-0038
NASA Ngr-05-020-103
ONR Nonr 225(83)
ARPA SD-87

Technical Objective:

To develop methods for the synthesis and construction of optical networks using birefringent crystals, and to build and test a particular network -- an achromatic wave plate for the visible spectrum.

Approach:

Theoretical work is directed toward the study of the sensitivity of the network transmission characteristic to crystal length, temperature, and angular aperture. Experimental work involves the construction and testing of achromatic wave plates.

Progress:

During the previous year achromatic quarter and half wave plates were assembled and tested. An achromatic quarter wave plate, for example, consisting of 6 sapphire crystals, each 1 mm thick, gave a retardation of 90° ±1° over the range from 4000 Å to 8000 Å. Achromatic half wave plates and wave plates using more than 6 crystals were also tested with equally good results. Also, methods for approximating the desired function better and extensions of the synthesis procedure were developed and used.

12. QUANTUM THEORY OF METALS

W. A. Harrison, Professor, Applied Physics

Research Associate:

A. O. E. Animalu

Graduate Students:

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C. J. Cooney
R. W. Shaw, Jr.
R. S. Sorbello

Agency Support:

ARPA SD-87

Technical Objectives:

The technical objectives of this program are to refine and apply the pseudopotential theory of simple metals and to seek analagous theories for systems for which the pseudopotential method is inapplicable. Refinements include the reformulation of Heine-Abarenkov theory and the inclusion of spin-orbit coupling. Applications have been made to optical properties, x-ray spectra, the concept of the metallic bond, diffusion and the theory of dislocations. Methods appropriate to transition metals are being sought.

Research Report:

Shaw and Harrison have completed the study of non-local effects in the Heine-Abarenkov method and a publication is in press concerning these effects and the relation to screening. The effort by Cooney to include spin-orbit coupling in the pseudopotential is near completion. It has been possible to retain the simplicity of the theory of the light metals by adding for the heavy metals a spin-orbit coupling form factor. We are seeking a simplified theory of the transition and noble metals based upon the resonant state concept for the treatment of d-bands; if successful this may lead to a theory of the electronic and

4. W. A. Harrison, "Electronic Structures and Soft X-Ray Spectroscopy," presented at Symposium on Soft X-Ray Spectroscopy, Glasgow, Scotland, Sept. 1967; to be published in the Proceedings of the Symposium on Soft X-Ray Spectroscopy, Academic Press (1968).

5. W. A. Harrison and A. Animalu, "Definition of an Optical Pseudopotential," presented at Americal Physical Society meeting in Chicago, March, 1967; Bull. Am. Phys. Soc. 12 415 (1967).

6. R. W. Shaw, Jr. and W. A. Harrison, "Reformulation of the Screened Heine-Abarenkov Model Potential," Phys. Rev. 163 (3) 604-611 (Nov. 1967).

7. A. Animalu, "The Pressure Dependence of the Electrical Resistivity, Thermopower and Phonon Dispersion in Liquid Hg," presented at International Conference on the Properties of Liquid Metals, Upton, New York; Advanc. Phys. 16, 605 (1967).

8. A. Animalu, "The Phase Transition in Ca, Sr and Ba Under Pressure," Phys. Rev. 161, 445 (1967).

9. A. Animalu, "The Optical Conductivity of Simple Metals," Phys. Rev. 163 (3) 557-561 (Nov. 1967).

10. A. Animalu, "Self-Consistent Theory of Optical Transitions in Simple Metals," Phys. Rev. 163 (3) 562-566 (Nov. 1967).

11. W. A. Harrison, "Parallel-band Effects in Interband Optical Absorption," Phys. Rev. 147 (2) 467-469 (July 1966).

12. A. O. E. Animalu, "The Total Electronic Band Structure Energy for 29 Elements," Proc. Roy. Soc. (London A) 294, 376 (1966).

13. A. O. E. Animalu, V. Heine, and B. Vasvari, "The Electronic Structure of Ca, Sr, and Ba Under Pressure," Phys. 154, 535 (1967).

2. H. Sonnenberg, "Note on Optical Second Harmonic Generation in Metals," Canadian Journal of Physics, December 1967.

3. H. Heffner and H. Sonnenberg, "Experimental Study of Optical Second Harmonic Generation in Silver," to be published in the Journal of the Optical Society of America.

14. PARTICLE IONIZATIONS IN SEMICONDUCTOR DETECTORS AND SCINTILLATION CRYSTALS

R. Hofstadter, Professor, Physics

Professional Associates:

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Agency Support:

AF 49(638)-1499
ONR Nonr 225(67)
ARPA SD-87

Technical Objective:

A fundamental investigation of the energy loss and pulse formation mechanism in alkali halide scintillation crystals and in silicon and germanium radiation detectors yields information on the intrinsic detector material properties. Results of this investigation also enable applications of these detectors to be extended to laboratory and space experiments at both very low and very high energies.

Approach:

The low energy investigations to date have utilized X-rays with energies from 3 to 1000 keV. Research in the near future will also utilize electrons with energies from about 3 to 800 keV. At the high energy end of the spectrum electrons with energies from 150 to 750 MeV produced in the Mark III Linear Accelerator have been used. Protons with energies from 15 to 400 MeV and positive pi-mesons with energies from 50 to 250 MeV which are released or produced in the target material by the high energy electrons have also been used as probes of the

detector material.

A fully demountable X-ray tube and a single crystal vacuum monochromator have been designed and constructed specifically for this investigation. A pulsed electron gun which can be mounted within the vacuum X-ray monochromator is presently under construction and nearing completion.

X-rays and electrons from naturally radioactive sources and from the monochromator and electron gun, respectively, and high energy particles from the Mark III Linear Accelerator are used in conjunction with specially developed techniques built around fast gun pulsing and digital signal averaging procedures to probe the pulse production and energy loss properties of the materials.

Research Report:

(1) The Fluorescent Response of NaI(Tl), CsI(Tl), CsI(Na) and CaF_2(Eu) to X-Rays and Low Energy Gamma Rays

The fluorescent response functions of NaI(Tl), CsI(Tl), CsI(Na) and CaF_2(Eu) have been determined with thin crystals over the energy range from 3.3 keV to 840 keV. A pronounced nonlinear dependence on photon energy has been observed in this region for all four types of crystals investigated. Qualitatively the response functions for NaI(Tl), CsI(Tl) and CsI(Na) are similar down to a photon energy of about 20 keV, but major differences are observed at lower energies. The response function of CaF_2(Eu) is very different from the response functions for the other three crystals over the entire energy range examined. Both K-shell and L-shell absorption edge discontinuities are evident in the fluorescent response curves for NaI(Tl) and CsI(Tl). Only K-shell absorption edge discontinuities could be observed in the response curves for CsI(Na) and CaF_2(Eu). Discontinuities in the spectral resolution function are observed in NaI(Tl) at energies corresponding to both the K-shell and L-shell absorption edges of iodine. A shift toward longer wavelengths in the light spectrum emitted by NaI(Tl) in response to excitation by X-rays with energies

below about 10 keV may also be indicated by photo-multiplier-dependent differences observed only at the lowest energies.

The nonlinear fluorescent response functions for these crystals indicates a corresponding nonlinear fluorescent dependence on electron energy. These electron response functions will be unfolded theoretically from the measured X-ray response functions, and will be normalized directly by measurements taken with electrons from naturally radioactive sources and from the electron gun.

(2) Charge Collection Efficiencies for Lithium-Drifted Silicon and Germanium Radiation Detectors in the X-Ray Energy Region

The linearity of the collected charge/keV has been determined as a function of energy between 4.9 and 75 keV for cooled lithium-drifted silicon detectors. Nonlinear effects for applied field intensities up to 1 kV/cm have been observed to extend to photon energies above 30 keV. Extrapolation to infinite fields does not remove the nonlinear effects for photon energies below 10 keV, indicating an intrinsic nonlinear response at low energies. The charge conversion factor appears to be independent of energy within 0.2% down to 10 keV. The same investigation is presently being extended to lithium-drifted germanium.

Theoretical calculations have shown that intrinsic nonlinearities of the type which we observe can be caused by charge trapping effects within the material. A comparison of theory and experiment for lithium-drifted silicon indicates that in addition to a probable different trapping lengths for electrons than for holes, there are nonuniform trap distributions within the material, with a special concentration towards the n^+ surface.

(3) Energy Loss in Lithium-Drifted Silicon and Germanium by High Energy Charged Particles

The energy loss functions in lithium-drifted silicon at room temperature and at 77 degrees Kelvin have been measured for protons over the energy range from 15 to 400 MeV; for electrons over the energy

range from 150 to 750 MeV; and for positive pi-mesons with energies from 50 to 250 MeV. The charge conversion factor ϵ for each particle type is presently being deduced at both temperature ranges from the experimental data. These results will be compared with values obtained by other workers and at lower energies.

The energy spectra were also measured with precision for each particle type. Landau spectra are presently being run by computer for normalized comparisons with the observations.

Similar measurements for energy loss functions at high energies are planned for lithium-drifted germanium detectors.

Reference Publications and Presentations:

1. D. W. Aitken and J. Lee, "A Fully Demountable X-Ray Tube for Vacuum Spectroscopy," W. W. Hansen Laboratories Report, HEPL-390 (1965).

2. D. W. Aitken, A. I. Marcum, and H. R. Zulliger, "Technique and Apparatus for Determining the Response of Scintillators and Semiconductors to Low Energy X-Ray Excitation," IEEE Trans. Nucl. Sci. NS-13, 287 (1966).

3. D. W. Aitken, B. Beron, G. Yenicay, and H. R. Zulliger, "The Fluorescent Response of NaI(Tl), CsI(Tl), CsI(Na) and CaF_2(Eu) to X-Rays and Low Energy Gamma Rays," IEEE Trans. Nucl. Sci. NS-14, 468 (1967).

4. H. R. Zulliger and D. W. Aitken, "The Linearity of the Charge Conversion Function for Cooled Lithium-Drifted Silicon Detectors in Response to X-Ray and Low Energy Gamma Ray Excitation," IEEE Trans. Nucl. Sci. NS-14, 563 (1967).

5. D. W. Aitken, D. W. Emerson, and H. R. Zulliger, "Energy Loss in Lithium-Drifted Silicon by High Energy Charged Particles," presented at the 14th Nuclear Science Symposium (October 1967); to be published in the IEEE Trans. Nucl. Sci.

6. H. R. Zulliger and D. W. Aitken, "Charge Collection Efficiencies for Lithium-Drifted Silicon and Germanium Detectors in the X-Ray Energy Region," presented at the 14th Nuclear Science Symposium (October 1967); to be published in the IEEE Trans. Nucl. Sci.

15. IMPERFECTION TRANSPORT AND CONTROL IN SOLIDS

R. A. Huggins, Professor, Materials Science

Professional Associates:

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Graduate Students:

L. D. Clark
R. W. Helliwell

Agency Support:

AEC AT(04-3)298
ARPA SD-87
ONR N14-67-A112-0020

Research Report:

(1) Use of Nuclear Magnetic Resonance Techniques to Study Defects and Transport in Solids

Graduate Student: L. D. Clark

The use of the observation of the temperature dependence of the width of nuclear magnetic resonance lines has been applied to the study of self diffusion in aluminum in the presence of substitutional impurities, and self diffusion in LiF doped with divalent impurities. From these latter results information was obtained concerning the association of vacancies with such impurities. These techniques have also been used to study the motion of Li^7 in a variety of oxides. In addition, studies of chemical shifts and quadrupole effects have been undertaken on a number of oxide systems containing vanadium in order to obtain information concerning their defect structure.

Apparatus is being designed and constructed to use pulsed NMR techniques to study ultra-slow motion of ions in solids, with particular interest in transport processes involving associated defects.

(2) Structural Control by the Use of Solid State Electrochemical Transducer Techniques

Graduate Student: R. W. Helliwell

Elevated temperature solid state electrochemical cell techniques are being developed to characterize and control the point defect structure of semiconductors and insulators.

Primary effort is now directed toward studies of the ionic transport properties of potential solid state electrolytes or transducers, particularly difluorides with the fluorite and rutile structures, and oxides with the beta alumina structure.

Reference Publications and Presentations:

1. T. W. Barbee, Jr., R. A. Huggins, and W. A. Little, "Effects of Dislocation Distribution on the Low Temperature Electrical Transport Properties of Deformed Metals," Phil. Mag. 14, 225-274 (Aug. 1966).

2. M. L. Rudee and R. A. Huggins, "Grain Boundary Segregation and the Cold-Work Peak in Iron Containing Carbon or Nitrogen," Trans. AIME 236, 1662-1666 (Dec. 1966).

3. M. P. Gomez, D. A. Stevenson, and R. A. Huggins, "Self Diffusion of Lead and Tellurium in Lead Telluride," presented at the Annual Meeting of the AIME, Los Angeles, Feb. 1967.

4. T. G. Stoebe, "Influence of OH^- Ions on Infrared Absorption and Ionic Conductivity in Lithium Fluoride Crystals," J. Phys. Chem. Solids 28, 1375-1382 (Feb. 1967).

16. EXPERIMENTAL AND FIELD INVESTIGATIONS OF THE DEFORMATION AND FRACTURE OF GRANITIC ROCKS

A. M. Johnson, Assistant Professor, Mineral Engineering and Geology

Graduate Students:

R. D. Lawrence
S. D. Peng

Technical Objective:

To investigate mechanical behaviors of quartz and feldspar and to understand how these two minerals interact to produce observed mechanical behaviors of granitic rocks.

(1) Process of Propagation of Fractures in Granitic Rocks

Graduate Student: S. N. Peng

Microfractures have long been recognized in granitic rocks, but their origin and significant effect on the rocks have not been explained. Several lines of evidence seem to indicate that microfractures in quartz grains largely control the gross fracture of granites. For example, it is well known to quarrymen that most granites split preferentially along quasi-perpendicular directions, called rift, grain, and hardway, in order of ease of splitting. Oriented samples of granite from a quarry in Massachusetts will be loaded to different stages of failure so that propagation and coalescence of microfractures can be studied. Mechanisms of failure and effects of anisotropic distribution of microfractures are being investigated. In conjunction with the laboratory investigation, the configuration of the quarry from which the rock samples were taken and the state of stress in the vicinity of the quarry will be measured to assist with modifications of quarry design to minimize rockbursts.

(2) Significance of Glide Lamellae in Plagioclase Feldspars.

Graduate Student: R. D. Lawrence

Glide lamellae in plagioclase are analogous to twin lamellae in calcite and dolomite. Analyses of orientations of these latter have proved to be a valuable tool for deciphering directions of principal strain in some rocks deformed naturally and experimentally. But most granitic rocks do not contain appreciable calcite or dolomite, whereas they contain abundant plagioclase.

Study of orientations of directions of gliding in plagioclase in granitic rocks adjacent to a fault in northern Washington seems to indicate a consistent deviation between the trends of maximum principal strain and the trend of the fault. A procedure is being developed for evaluating the influence of strain alone on twinning, by experimentally deforming samples of several members of the plagioclase solid-solution series and samples of plagioclase-bearing rocks with known initial fabrics.

17. BULK EFFECTS IN SEMICONDUCTORS

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Professional Associates:

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Agency Support:

AF 30(602)-3595
Army DA-28-043-AMC-00482(E)
NASA Ngr-05-020-165
ARPA SD-87

(1) Solid State Travelling Wave Amplifier

Technical Objective:

To realize a solid state space charge wave amplifier based on the Gunn effect and working in the frequency range from 0.5 to 2 Ghz.

Research Report:

A simple one dimensional theory predicts that in GaAs biased in the negative differential mobility region, any space charge disturbance grows exponentially with distance, with a characteristic length depending on the resistivity of the material (typically 200 μ for 500 ohm-cm material). The time delay is to a first approximation independent of frequency and proportional to the applied voltage.

We have found experimentally that a reasonably strong space charge excitation can be achieved through an extra ohmic electrode in

the form of a thin strip 3 mils wide, located on one side face at a distance of 6 mils from the cathode contact. A similar strip electrode near the anode contact can serve as extracting contact and with such a configuration we were able to observe a net terminal gain of up to 5 db over a 60 MHz frequency band centered around 700 MHz, with one oscillating specimen, biased a few per cent below the oscillation threshold.

We have been working with GaAs, single crystal oxygen doped material of resistivity varying between 300 and 3000 ohm-cm. The crystal specimens were in the form of diodes roughly 1 mm^3 in volume with a pair of symmetrical ohmic contacts through which a dc bias field is set up.

The product: doping density times length of diode lies in the neighborhood of the critical nl product value of $10^{12} cm^{-2}$, which means that some of our specimens are unconditionally stable while others break into spontaneous oscillations at a high enough voltage. In all our rf measurements with oscillating samples the bias value was adjusted below the oscillation threshold.

Capacitative probe measurements of the dc potential across GaAs diodes with ohmic contacts produced results in agreement with the velocity field characteristic curve of Ruch and Kino. A non-uniform electric field distribution is established when average field is above threshold, due to space charge injections from the cathode contact.

We are presently trying to improve the coupling between rf signal and space charge wave and vice versa; in particular, to make it as broadband as possible since the amplification mechanism is to a first approximation independent of frequency.

(2) Transport Properties of Semiconductors

Technical Objective:

To determine the velocity and diffusion coefficient of carriers in semiconductors as a function of the electric field.

Research Report:

Recently coherent current oscillation and traveling high field

domains have been observed in n-type germanium in the range of temperature between 27°K and 120°K. Although the physical origin of these oscillations are as yet uncertain they seem to be strongly related to the velocity field characteristic.

The method used for such studies is similar to that employed in the past for the determination of the transport properties of the electrons in GaAs. The response of a reversed biased Schottky barrier-i-n^+ Ge device to a short pulse (0.1 ns) of high energy electrons was measured. The incident electrons create a sheet of charges in the semiconductor very close to the cathode. The electrons are swept, under the influence of the nearly uniform bias field, towards the anode. As the electrons traverse the field region, a constant current is induced in the external circuit. The induced current persists as long as the electrons are in the field region. The width of the induced current pulse is then a measure of the transit time of the electrons. With a knowledge of the width of the field region (i-layer), the drift velocity corresponding to the particular bias field can be accurately determined.

The devices were fabricated from high purity, high resistivity n-type Ge (carrier concentration approximately 6×10^{11} at 195°K) cut in the (100) direction. In operation, the devices were cooled by continuously transferring cold helium gas from a liquid helium storage dewar. The device temperature was measured with a copper-constantan thermocouple placed next to it. Liquid nitrogen was used as the reference junction temperature.

The velocity field characteristic of electrons in germanium was measured in a range of temperatures between 33°K and 130°K and the electric field above the (100) orientation of the crystal. At 33°K a negative differential mobility of 300 cm^2/V sec was observed with a threshold field of 1.5 kV/cm. The negative differential mobility decreases with increasing temperature. At 130°K there is definitely no negative differential mobility.

(3) Carrier Wave Studies in Indium Antimonide

Technical Objective:

To study the propagation of carrier waves in InSb subject to crossed electric and magnetic fields.

Research Report:

We have been performing what we believe to be the first measurements of carrier waves in a solid. A carrier wave is the solid state counterpart of a space charge, well known in the microwave tube field. Normally such waves are heavily dampened even at the highest microwave frequencies because of collisional damping. Theoretical studies carried out here at Stanford have indicated that an electron carrier wave can have low loss, and even gain, provided a transverse (to the carrier drift) magnetic field and a background of holes are present. We have found that InSb at 200°K is an excellent material in which to observe these waves. To date, measurements have been performed in a magnetic field of about 2 kilogauss and frequencies from 10 to 45 MHz. Phase velocities of the order of 10^6 cm/sec and losses of less than 1 db/wavelength have been measured thus far.

Reference Publications:

1. V. Hamza and G. S. Kino, "The Accuracy of Numerical Solutions for Electron Gun Design," Microwave Laboratory Report No. 1423, Stanford University (Mar. 1966); to be published in J. Appl. Phys.

2. G. S. Kino, "The Excitation of a Probe Placed Near a Semiconductor," Proc. IEEE 55, 90-92 (Jan. 1967).

3. J. M. Owens and G. S. Kino, "Multiple Current Spiking in Long Gunn Oscillators," Phys. Letters 23 (7) 453-455 (Nov. 1966).

4. J. G. Ruch and G. S. Kino, "Measurement of the Velocity-Field Characteristic of Gallium Arsenide," Appl. Phys. Lett. 10, 40-42 (Jan. 1967).

5. B. E. Burke and G. S. Kino, "Helicon Wave Propagation in InSb," Microwave Laboratory Report No. 1537, Stanford University (May 1967).

6. P. N. Robson, G. S. Kino, and B. Fay, "Two Port Microwave Amplification in Long Samples of GaAs," Microwave Laboratory Report No. 1553, Stanford University (July 1967); to be submitted to IEEE Trans. ED.

7. K. J. Harker, G. S. Kino, and D. Eitelbach, "Longitudinal Oscillations in Bounded One-Dimensional Nonuniform Plasmas," Microwave Laboratory Report No. 1563, Stanford University (July 1967); submitted to Physics of Fluids.

8. K. J. Harker and H. J. Shaw, "Transient Spin Wave Buildup in Ferrites," J. Appl. Phys. 37, 3035-3043 (July 1966).

9. K. J. Harker, "Computer Program for the Gunn Effect," Microwave Laboratory Report No. 1455, Stanford University (July 1966).

10. K. J. Harker, "Numerical Solution of the Gunn Effect Equations," Microwave Laboratory Report No. 1463, Stanford University (Aug. 1966); submitted to IEEE Trans. ED.

18. CO-OPERATIVE PHENOMENA IN SOLIDS, LIQUIDS AND GASES

W. A. Little, Professor, Physics

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S. T. Spence
S. T. Wang

Agency Support:

ONR Nonr 225(76)
NSF GP 6336
ARPA SD-87
Army DAHC04-67-C-0014

Technical Objectives

To study the properties of many-body systems such as superconductors, superfluids, macromolecules through the observation of those properties derived from the collective or co-operative behavior of the constituent particles.

Approach:

A joint theoretical and experimental study is being made of several problems relating to the possibility of superconductivity occurring in organic macromolecules, studies of the collective motion of electrons in dyes and polyacenes and the screening effects produced by this motion; an investigation of the zero-sound mode in He^3 by a study of the temperature dependence of the cross-section for scattering

X rays from the liquid; the operation of a low-temperature target assembly for producing polarized nuclei for experiments on high energy electron scattering; a study of the photo-electric effect in normal and superconducting metals, the lifetime of persistent currents in superconductors and the Abrikosov vortex array of persistent currents in superconductors and the Abrikosov vortex array in Type II superconductors.

Research Report:

Work has continued on the problem of one dimensional superconductivity. We have shown theoretically that the dimensionality does not preclude the existence of superconductivity in a linear chain but that the transition to the highly conducting state is smooth and somewhat depressed in temperature.(1) Detailed molecular orbital calculations have been made of Coulomb screening in linear conjugated molecules and in planar conjugated molecules. In the linear molecules Friedel oscillations dominate the behavior and mask any screening while in planar molecules significant screening does occur. Experiments to test these conclusions by energy-loss measurements are being set up. Calculations have also been made on the possibility of a Cooper type instability of the normal Hartree-Fock state in tetra-dye substituted porphines. Some of the essential matrix elements needed to test the computed values can be derived directly from experiment. An inelastic electron-diffraction experiment is being built up to determine these parameters directly.

Work has continued on determining the velocity of high frequency sound in liquid He^3 by small angle X ray scattering.(2,3) The zero sound mode predicted by Landau has been observed and thermal quenching of this mode is now being studied. Good agreement with the hydrodynamic velocity of low frequency sound has been obtained at temperatures above 0.8°K. Measurements are being extended to larger angles for measurements of the Fermi momentum of He^3 and to lower temperatures with the use of a dilution refrigerator.

An electron mirror microscope has been built to study the pinning and crystallinity of the Abrikosov vortex array in Type II superconductors. Deflection plates for positioning the beam and improvements in the beam optics have been made in the last year and calibration studies made of the magnification under various modes of operation. Observations have been made of samples of Sn and Pb in the intermediate state.

The vortex array has also been studied by measurements of the impedance of thin film superconductors in a magnetic field normal to the surface. Possible device applications of these materials have been discussed[4] and good agreement with a simple theoretical model has been obtained. This work has tied in with other experiments where we have endeavored to fabricate extremely fine superconducting wires to measure the decay of persistent currents. Techniques to do this are being developed.

To study the far infra-red absorption of fine linear superconductors where low lying plasmon states are expected, an electron cyclotron resonance maser has been designed and is under construction. Using a 50K gauss, room temperature access superconducting magnet which was constructed for this purpose, power of the order of watts should be developed at 2 mm wavelength and several milliwatts at the first harmonic at 1 mm.

Progress has been made in an experiment to determine the small difference in threshold for the photoelectric effect between normal and superconducting metals. Work has continued on the polarized holmium experiments.[5,6]

Reference Publications:

1. W. A. Little, "Decay of Persistent Currents in Small Superconductors," Phys. Rev. 156, 396 (1967).

2. N. P. Shah, "X-Ray Scattering by Zero-Sound Phonons in Liquid Helium-3," Bull. Amer. Phys. Soc. 2 (7) 900 (Dec. 1966).

3. N. P. Shah, "Determination of the Velocity of High Frequency Sound in Liquid Helium-3 by X Ray Scattering," (to be published).

4. W. A. Little, "Device Application of Superinductors," presented at Symposium on the Physics of Superconducting Devices, Charlottesville, Va. (1967) (to be published).

5. T. R. Fisher, R. S. Safrata, E. G. Shelley, J. McCarthy and S. M. Austin, "Interaction of Fast Neutrons with Oriented Ho^{165}," Phys. Rev. 157, 1149 (May 1967).

6. R. S. Safrata, T. R. Fisher, E. G. Shelley, "Magnetic Hysteresis of Holmium Metal at 4.2°K," J. Appl. Phys. 37, 4869-4872 (Dec. 1966).

7. T. R. Fisher, E. G. Shelley, R. S. Safrata, J. McCarthy, and R. C. Barrett, "Spin-Spin Interaction in the Total Cross Section for Polarized 7.85-MeV Neutrons on Polarized Ho^{165}," Phys. Rev. Lett. 17, 1 (July 1966).

19. REACTIVITY OF SOLIDS

R. J. Madix, Assistant Professor, Chemical Engineering

Graduate Students:

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J. A. Schwarz
A. A. Susu

Agency Support:

NSF GK 826
ARPA SD-87

Technical Objective:

To elucidate the kinematics of reactive gas-solid collisions and the role of energy transfer therein.

Research Report:

(1) Energy Accommodation in Heterogeneous Atom Recombination

Graduate Students: C-m. J. Lee
G. A. Melin

The fraction of the heat of reaction, β , which is transferred to the substrate on which hydrogen atoms from the gas phase recombine is being investigated. The atoms are formed by an r-f discharge and allowed to diffuse down a side-arm where they recombine on a metal filament. The atom concentration profile, as determined by Wrede-Harteck gauges, reveals the probability of recombination and allows calculation of the flux of atoms striking the filament surface. Simultaneous measurement of the power input to the wire due to recombination allows the determination of β. The dependence of β on material properties is to be investigated.

In order to investigate the practical limitations of the Wrede gauges, their response to atoms of oxygen, nitrogen and hydrogen

is being compared with atom concentrations determined by a gas-phase chemical titration procedure. A flow-discharge tube is employed for this purpose. The gauge response to oxygen atom concentrations from zero to forty percent at pressures between 50 and 250 is currently being studied with the NO_2 titration.

Concurrent to the characterization of the gauges, the system is being modified for use as a diffusion tube. The design will allow intermittent calibration of the gauges by the flow-discharge method described above.

(2) High Temperature Reaction of Solids

Graduate Students: R. A. Korus
J. A. Schwarz
A. A. Susu

Molecular beam, low energy electron diffraction and electron microscopic techniques are being utilized to elucidate the kinetics and reactive collision process occurring in high temperature gas-solid reactions. In particular, reactions are being studied in which the reaction products vaporize. These products can be detected mass spectrometrically. If the reactant gas is directed as the surface under study in the form of a modulated molecular beam, the products can be phase detected. The product phase lag is directly related to the kinetic rate constant. Thus, the reaction sequence occurring on the surface can be elucidated.

The reaction of oxygen with heated germanium and silicon wafers was studied. The reaction of oxygen with (110)-oriented germanium wafers showed characteristics similar to the reaction with the (100) oriented wafers previously studied. The gas temperature coefficient for the reaction is quite small over an extended range of temperatures. Results with silicon have been obtained, but they are considered preliminary.

Many reactions of the type mentioned above lead to the formation of pits of well defined structure on the surface. We have employed LEED to demonstrate that pits with 4-fold symmetry form on the (100)

surface of germanium when it is oxidized at 750°C. The square pits have (100) faces. The size of these pits has been determined with the aid of the electron microscope. Investigations are currently being conducted to determine the nature of the sites which lead to pit formation.

20. CHEMICAL AND PHYSICAL PROPERTIES OF SOLIDS

H. M. McConnell, Professor, Chemistry

Professional Associates:

J. C. A. Boeyens
R. C. Davis
C. L. Hamilton
I. C. P. Smith

Graduate Students:

L. J. Berliner
W. J. Deal
R. M. Frost
F. R. Gamble
A. F. Horwitz
W. L. Hubbell
M. S. Itzkowitz
R. M. Metzger
R. T. Ogata
S. Ogawa
E. J. Shimshick
R. H. Young

Agency Support:

NSF GP 6346 and GB 4911
ONR Nonr 225(88)
ARPA SD-87

Research Report:

(1) Interactions Between Molecules and Superconductors

Technical Objective:

To attempt to prepare an alloy between molecules andmetals which have desirable superconducting properties including high temperature superconductivity.

Approach:

Codeposition of metal atoms and molecules in a high vacuum system onto a quartz substrate so as to prepare a molecular alloy.

Progress:

Aluminum films containing organic molecules were prepared by simultaneous deposition of the components on a cold surface. Superconducting critical temperatures as high as 5.24°K were observed, which represents an enhancement of 4°K over the normal bulk transition temperature of aluminum.

Reference Publications:

1. M. S. Itzkowitz, "Monte Carlo Simulation of the Effects of Molecular Motion on the EPR Spectrum of Nitroxide Free Radicals," J. Chem. Phys. 46 (8) 3048-3056 (Apr. 1967).

2. S. Ogawa and H. M. McConnell, "Spin-Label Study of Hemoglobin Conformations in Solution," Proc. Natl. Acad. Sci. 58 (1) 19-26 (July 1967).

3. H. M. McConnell and J. C. A. Boeyens, "Spin Label Determination of Enzyme Symmetry," J. Phys. Chem. 71 (1) 12-14 (Jan. 1967).

4. B. M. Hoffman, F. R. Gamble, and H. M. McConnell, "Interactions between Molecules and Superconductors," J. Amer. Chem. Soc. 89 (1) 27-30 (Jan. 1967).

5. H. M. McConnell, F. R. Gamble, and B. M. Hoffman, "Interactions between Superconductors and Organic Molecules," Proc. Natl. Acad. Sci. 57 (5) 1131-1137 (May 1967).

6. S. Ohnishi, J. C. A. Boeyens, and H. M. McConnell, "Spin-Labeled Hemoglobin Crystals," Proc. Natl. Acad. Sci. 56 (3) 809-813 (Sept. 1966).

7. J. C. A. Boeyens and H. M. McConnell, "Spin-Labeled Hemoglobin," Proc. Natl. Acad. Sci. 56 (1) 22-25 (July, 1966).

21. HOT ELECTRONS IN SEMICONDUCTORS

J. L. Moll, Professor, Electrical Engineering

Research Associates:

Y. Komiya
D. J. Ruzicka

Graduate Students:

D. M. Chang
W. E. Drummond
C-Y. Duh
Y-Z. Liu
W. L. Snyder
R. H. Weissman

Agency Support:

ONR Nonr 225(83)
ARPA SD-87

Technical Objective:

To measure electron drift velocities in semiconductors at high electric fields.

Approach:

Three materials are being studied: Si, Ge and GaAs. For GaAs we are using the transient photoresponse of GaAs P-I-N and Schottky barrier-I-N diodes. The response in the presence of trapping must be analyzed but it is nevertheless possible to relate response to electron velocity. For Ge, transit time in P-I-N diodes is used. The silicon measurements have been completed.

Research Report:

Our measurements of electron drift velocity in silicon have been completed and reported in two publications. We have obtained temperature dependence for $77°K < T < 400°K$. The relative values of

coupling to various phonon branches as well as absolute magnitude agree with results of low field measurements.

Reports of oscillations in n-type germanium has led to increased interest in this material. We have measured velocity from the transit time method in this material at 77°K with the result that the differential mobility is less than $\pm$ 0.02 μ where μ is the low field mobility. We are refining the 77°K measurements and extending the temperature to 4°K. The $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions are being studied.

The GaAs study has been hindered by lack of suitable intrinsic material. We have been evaluating the liquid growth as a possible method of getting ultra-pure GaAs. The best material is several times $10^{14}/cm^3$ density and density of $10^{12}/cm^3$ is required.

Reference Publications:

1. C. Y. Duh and J. L. Moll, "Electron Drift Velocity in Avalanching Silicon Diodes," IEEE Trans. on Elect. Dev., ED-13 (1) 63-67 (Jan. 1967).

2. C. Y. Duh and J. L. Moll, submitted to Solid State Electronics.

22. RELATION BETWEEN CRYSTALLINE IMPERFECTIONS AND THE PHYSICAL PROPERTIES OF CRYSTALS

W. D. Nix, Associate Professor, Materials Science

Research Associate: D. J. Dingley

Graduate Students:

E. V. Benton
W. A. Coghlan
R. Gasca-Neri
W. C. Harrigan
W. R. Johnson
B. L. Mattes
E. C. Muehleisen
H. W. Rosenberg
A. A. Solomon

Agency Support:

NSF GK 386
AEC AT(04-3)-326 PA17
ARPA SD-87

Research Report:

(1) Influence of Structural Inhomogeneities on the Magnetic Properties of High Purity Nickel

Graduate Student: W. R. Johnson

In order to study the effect of structural inhomogeneities such as dislocations and cells on the initial permeability and coercive force of high purity nickel, simultaneous measurements were made of magnetic properties (initial permeability and coercive force) and structural parameters (cell size and RMS strain measured with the X-ray peak broadening technique) in polycrystalline samples of high purity nickel.

A study was made of the Warren-Averbach X-ray peak broadening technique for determining RMS strain and cell size in cold worked metals. Computer programs were written which automatically make all

necessary corrections on experimental X-ray peaks and which yield Fourier coefficients for the peak shapes. Computer programs were also developed to calculate RMS strain and cell size from the Fourier coefficients. A goniometer device was designed and built to allow reflections of several types to be obtained even in heavily textured sheet. Mechanical working and heat treating techniques were designed to eliminate the effect of texture and allow an unambiguous correlation between RMS strain and cell size and the magnetic properties.

Measurements of line broadening and peak shape were made on pure nickel deformed 90% and recovered at 250°C. for up to 100 hours. Initial susceptibility measurements were also obtained for these samples thereby allowing the relationships between residual strain, particle size and initial susceptibility to be established. The initial susceptibility was found to be linearly related to the ratio of the square of the particle size to the RMS strain for recovery times up to two hours. At longer times the relationship was obscured by the onset of recrystallization. It was also found with transmission electron microscopy that most of the samples in the study contained some recrystallized grains. Thus, in spite of the fact that a simple (Kersten) internal strain theory can be constructed to yield a linear relation between the susceptibility and the ratio of the square of the cell size and the RMS strain, the experimental results may not be considered unambiguous.

In order to remove the ambiguity (partial recrystallization) encountered in the previous work, experiments have been planned and are underway to measure the magnetic properties and structural parameters in samples deformed at liquid nitrogen temperature. It is expected that the effects of recovery at room temperature will be large and easily controlled.

(2) A Study of the Ferroelectric Transformation in $BaTiO_3$

Graduate Student: R. L. Mattes

A general thermodynamic theory of the ferroelectric transformation in $BaTiO_3$ has been formulated. The theory is based on Landau's treatment of second order phase transitions and therefore leads to the prediction that the cubic tetragonal phase transformation in $BaTiO_3$ is a second order phase transition. The theory differs from that of Devonshire in that it treats both polarization and strain as separate but related quantities. To explain the discontinuous change in polarization at the actual transition temperature it is proposed that a prescient state exists below the true curie temperature and becomes unstable at the actual transformation temperature. In the prescient state the bulk of the material is under hydrostatic pressure while the surface layers provide that pressure by supporting a planar tensile stress. The surface layer in the prescient state is tetragonal and polarized while the bulk remains cubic. The theory quantitatively accounts for:

(1) The shift in the spontaneous transition temperature with stress,

(2) The surface layer which has been observed in the prescient state, and

(3) The low temperature phase transitions.

The theory qualitatively accounts for:

(1) The second order phase transition temperature,

(2) The spontaneous phase transition temperatures,

(3) The dependence of the permittivity and polarization on temperature, and

(4) The several anomalies associated with the transformation.

The ferroelectric transformation in $BaTiO_3$ single crystals has also been studied experimentally. A single phase boundary is produced in an oriented single crystal by placing the crystal in a temperature gradient. The position of the interface and the interface temperature are measured as a function of the temperature gradient and the rate of heating. The heating rate experiments indicate that the spontaneous transition temperature increases linearly with heating rate. It has

been shown that the effects of heating rate can be explained in terms of the thermal stresses which are imposed by the temperature gradients associated with heating. The effects of thermal stresses on the transition temperature are a natural product of the theory described above.

Numerical and computer techniques have been developed to calculate the local dipole electric field in dielectric materials with finite dimensions. Dipole field calculations have been made for solids with various sizes and shapes. A number of anomalies associated with the size and shape dependence of dielectric behavior can be explained on the basis of these calculations.

(3) A Study of Diffraction Contrast from Dislocations in Electron Microscopy

Graduate Student: W. A. Coghlan

The kinematical theory of diffraction contrast from dislocations in electron microscopy has been improved with the use of computer techniques. The oscillating term contribution to the scattered amplitude (originally neglected by Hirsch) has been included in this treatment. It is found that because of the oscillating term, the simple rule that dislocations are invisible when $\vec{g} \cdot \vec{b} = 0$ does not always work. The complete kinematical theory predicts that when $\vec{g} \cdot \vec{b} = 1$, screw dislocations will become invisible for certain foil thicknesses, Bragg angle deviations and dislocation positions in the foil.

An experimental study of invisibility criteria for dislocations has been carried out using dislocation networks in thin foils of iron. The use of Frank's rule for junctions allows the Burgers vectors of the dislocations in the networks to be determined unambiguously with multi-reflection dark field electron microscopy. The results of both bright and dark field microscopy indicate that dislocations become invisible for certain Bragg angle deviations even when $\vec{g} \cdot \vec{b} = 0$. Tilting experiments have shown that dislocations which are visible at $s = 0$ become invisible when the Bragg angle deviation reaches a critical range of values. The dislocations are again visible at very

large Bragg angle deviations. The invisibilities occur in the dynamical range and cannot be explained by the kinematical theory. Dynamical calculations of the contrast from screw dislocations have been carried out and the conditions of invisibility which have been observed are predicted.

A generalized computer program has been developed to compute contrast from dislocations under various conditions. The program is based on the dynamical theory and can treat imperfect dislocations as well as the associated stacking faults. The program is also capable of computing contrast from dislocation arrays and is currently being used in research.

(4) The Interaction of Highly Ionizing Charged Particles with Polymers

Graduate Student: E. V. Benton

This program involves a study of the characteristics of charged particle tracks in polymers and the engineering aspects of particle track identification with polymers. Suitable polymeric materials have been irradiated with fission fragments from Cf^{252}. Tracks have been observed and monitored with chemical etching and decoration techniques and, in addition with optical and electron microscopy.

Several experiments have been carried out using beams of heavy particles generated in the heavy ion linear accelerator at the Lawrence Radiation Laboratory at Berkeley. Characteristics of the tracks of these particles have been studied in various polymers as a function of their charge and energy.

Theoretical calculations have been made of range-energy and energy-loss relationships for multi-charged heavy ions of energies from 10^{-1} to 10^{3} Mev/emu. These calculations are in good agreement with experimental measurements.

A criterion for charged particle track formation in polymers has been formulated. It is based on the concept of restricted rate of energy loss in the region of the track. According to this theory the

charged particle loses its energy by producing δ rays with a range of energy. The damage which creates the track is produced by low energy δ rays ($< 10^3$ Mev). It is proposed that high energy δ rays ($> 10^3$ Mev) are sufficiently energetic to leave the vicinity of the track (and the sample too) and are thus ineffective in producing track damage. The proposed registration criterion is in excellent agreement with registration experiments on cellulose nitrate.

Practical aspects of the use of polymers as charged particle detectors are also being investigated. Their use for the identification of slow heavy particles has been found satisfactory. However, they have not yet been found suitable for the detection of heavy relativistic particles.

(5) An Investigation of the Austenite - Martensite Phase Transformation in Ferrous Alloys Using Transmission Electron Microscopy

In order to obtain data on the mechanism of the austenite - martensite phase transformation, thin foils of an Fe-30% Ni - 0.01% C alloy, partially transformed to martensite, have been used to identify the Burgers vectors of dislocations both in the martensite and in the austenite ahead of the phase boundary. Experiments have failed to show whether the dislocations ahead of the advancing boundary are swept up by the boundary or whether they can pass through the boundary and become incorporated into the martensite phase.

The mid-rib in the martensite plates has been identified as being a region of high twin density. The twins are very thin, less than 100 Å, and are closely associated with dislocation slip bands lying in the twin plane.

Careful studies of dislocation and twin contrast in the electron image have indicated that the martensite plate grows by the nucleation and subsequent coalescence of twins in the austenite in the vicinity of the martensite plate. The mid-rib plane appears to be a consequence of the nucleation and growth mechanism and thus may not be crystallographically significant.

(6) A Study of Creep and Stress Relaxation in Crystalline Solids

(a) Measurement of Dislocation Velocities at Elevated Temperatures

Graduate Students: A. A. Solomon
F. F. M. Lee (with Professor Shyne)

Stress relaxation techniques are being used to obtain information about dislocation velocities in single crystal and polycrystalline samples of Fe - 3.0% Si at elevated temperatures (500°C - 800°C). The experiments are being carried out with the use of an electronically controlled MTS hydraulic testing machine. The instrument allows the length of a sample to be maintained constant during a relaxation to within one microinch. Because of this precise control the elastic constant of the machine is simply the elastic constant of the sample being tested. In addition, the use of this instrument (as opposed to the more conventional mechanical machines) allows changes in mode (load or position control) to be made almost instantaneously.

Preliminary results of stress relaxation experiments indicate that the stress dependence of the relaxation process may be written either as $\dot{\epsilon} = A \exp B\sigma$ or $\dot{\epsilon} = A'\sigma^n$. The activation volumes obtained from the relaxations are consistent with the jogged screw dislocation theory for high temperature deformation. However, the fact that the relaxations also follow a power law stress dependence leads one to suspect that the stress relaxation may simply represent a variable stress creep test with all of the attendant structural changes. This simple view cannot be easily accepted since significant stress relaxation takes places in a few seconds. It is difficult to imagine that significant structural changes can take place in such a short period of time.

Several experiments are under way to clarify the meaning of the stress relaxation results. Two of the more critical experiments are:

(1) Measurement of activation volumes by measuring the stress dependence of the activation energy for creep.

(2) Measurement of dislocation density and cell size as a function of stress relaxation. (The mode control facility available on the MTS machine makes meaningful structural measurements possible.)

The use of the MTS machine allows relaxations tc be run during a creep test as well as during a tensile test. This feature will allow for the first time a comparison of the dynamics of creep deformation with the dynamics of plastic flow during a tensile test.

Direct measurements are being made of dislocation velocities in LiF at elevated temperature (100°C - 200°C). The technique involves a measurement of the kinetics of annihilation of a single dislocation dipole produced in a single crystal of LiF by an indentation process. A crystal containing an isolated dipole is heated to an elevated temperature. After a short period of time the crystal is cooled to room temperature and the dipole separation distance is remeasured and the average velocity computed from the change in separation distance. The stress in this experiment is computed from the mutual stress field interaction of the two dislocations.

The results of the dipole annihilation experiments indicate that the dislocation velocity in LiF at elevated temperatures depends linearly on the stress. This result is in sharp contrast to the room temperature results of Johnston and Gilman, but is consistent with low stress experiments in NaCl. Stress relaxation experiments will be carried out to determine whether the stress relaxation technique can be expected to accurately reveal the stress dependence of the dislocation velocities at high temperatures.

A thermodynamic treatment of the annihilation of dislocation loops has led to a new technique for determining the self stresses and self forces in dislocation loops having equilibrium shape. According to this analysis, the self forces in an equilibrium shaped loop are equal for all parts of the loop and are easily calculated by computing the variation of the elastic energy of the loop with respect to loop area at constant loop shape.

(b) Creep and Strees Relaxation in Single Crystals of LiF

Graduate Student: W. A. Coghlan

Creep and stress relaxation experiments are being carried out in single crystals of LiF. It is expected that the mechanism of creep may

be identified in this material because of the degree to which the important variables may be controlled and measured (eg: dislocation density, purity, orientation). In addition, the dipole annihilation experiments have provided information about the stress and temperature dependence of dislocation velocity. It is therefore expected that an unambiguous determination of the controlling mechanism for creep can be made in this material. Since other work indicates that the stress and temperature dependence for creep of polycrystalline NaCl is very similar to that for metals, it is expected that results on LiF will be applicable to metallic systems.

(c) Influence of "C + A" Slip on the Basal Creep Behavior of Hexagonal Metals

Basal creep in Zn is characterized by a very small activation energy and a very large stress dependence. It has been suggested that this behavior is caused by the lack of non-conservative jogs in the basal dislocations. Experiments are underway to produce a forest of "c + a" dislocations. Since "c + a" dislocations have Burgers vectors with a component normal to the basal plane, it is expected that they will be effective in producing non-conservative jogs in the basal dislocations. Basal creep experiments will be carried out on single crystals of Zn which contain "c + a" dislocations. It is expected that the stress and temperature dependence will be greatly changed by the formation of the forest.

(d) Mechanisms of Creep in Nickel Based Solid Solutions

Graduate Students: W. C. Harrigan
W. R. Johnson

A program of research has been initiated to determine the important factors which control the creep properties of nickel based solid solutions. The Ni-W solid solution has been chosen for study because of its practical importance (refractory metal alloying additions are an important component of superalloys) and because the addition of W is expected to cause large changes in the high temperature mechanical

properties. Also, the large difference in the scattering factors of Ni and W makes the X-ray determination of the structure of the solid solution possible.

Of particular interest in this study is the stress and temperature dependence of steady state creep and the influence of solid solution alloying additions on these parameters. Separate measurements of the dynamic elastic modulus of Ni-W alloys at elevated temperatures and the effect of W on the stacking fault energy are being made. Preliminary results indicate that the dynamic elastic modulus is almost independent of W content and that the effect of W on the creep properties cannot be found in the elastic modulus. Preliminary findings indicate that additions of W decrease the stacking fault energy of nickel and that the high temperature strength of Ni-W alloys may be due to low stacking fault energy. Experiments are currently underway to document the effects of W on the creep properties and to measure the relevant structural features.

(e) The Structure Dependence of Viscous Deformation in Metals

Graduate Student: E. C. Muehleisen

A dislocation climb model of viscous creep has been formulated. Experiments are now underway to test the predictions of the model. Of particular interest is the dependence of viscous creep on the defect structure of metals. Experiments are being carried out to determine the influence of 1) dislocation density, 2) stacking fault energy, 3) second phase inclusions, and 4) sample size on the stress and temperature dependence of viscous creep. Preliminary results indicate that a well developed cell structure is formed in aluminum samples which have been deformed a few percent under viscous deformation conditions.

(7) Deformation Mechanisms in Titanium Alloys

Graduate Student: H. W. Rosenberg

A study of deformation mechanisms in titanium and titanium-aluminum alloys is being initiated. Preliminary work involved the use of transmission electron microscopy to determine the microstructural

features responsible for strengthening. Later work will involve a detailed study of the more important strengthening mechanisms.

Reference Publications:

1. W. D. Nix, "On the Jogged Screw Dislocation Model for Steady State Creep," Acta Met. 15 (6) 1079-1080 (June 1967).

2. M. E. Gulden and W. D. Nix, "Observations of Dislocation Sources in an Aluminum-Copper-Silicon Alloy," (accepted for publication in Phil. Mag.).

3. W. A. Coghlan and W. D. Nix, "Contributions to the Kinematical Theory of Diffraction Contrast from Screw Dislocations," (submitted to Phil. Mag.).

4. K. Nishioka and W. D. Nix, "A Statistical Thermodynamic Treatment of Jogs on Screw Dislocations," (submitted to J. Appl. Phys.).

Reference Reports:

1. W. R. Johson, "Effects of Recovery on the Initial Magnetic Susceptibility of Plastically Deformed High Purity Nickel," SU-DMS Master's Report No. 66-11 (Dec. 1966).

2. W. D. Nix, "On the Jogged Screw Dislocation Model for Steady State Creep," SU-DMS Report No. 66-41 (Dec. 1966).

3. W. D. Nix, "On the Stress Dependence of the Dislocation Density During Steady State Creep," SU-DMS Report No. 66-42 (Dec. 1966).

4. M. E. Gulden and W. D. Nix, "Observations of Dislocation Sources in an Aluminum-Copper-Silicon Alloy," SU-DMS Report No. 67-3 (Jan. 1967).

5. K. Nishioka and W. D. Nix, "A Statistical Thermodynamic Treatment of Jogs on Screw Dislocations" SU-DMS Report No. 67-29 (July 1967).

6. W. A. Coghlan and W. D. Nix, "Contribution to the Kinematical Theory of Diffraction Contrast from Screw Dislocations in the Electron Microscope," SU-DMS Report No. 67-34 (Aug. 1967).

23. STIMULATED RAMAN EFFECT

R. H. Pantell, Professor, Electrical Engineering

Graduate Students:

W. R. Callen, Jr.
J. A. Gelbwachs
B. G. Huth
R. L. Kohn
P. W. Pheneger, Jr.
H. E. Puthoff
J. Warszawski
S. S. Sussman

Agency Support:

ONR Nonr 225(48)
AF 33(615)-3670
NSF GK 616
ONR N00014-67-A-0112-0018

Technical Objectives:

To study the behavior of the stimulated Raman effect inside an external resonator; to study Raman scattering from transitions which are infrared active.

Approach:

Stimulated Raman emission has been generated in an external resonator using a Q-switched laser. The apparatus is constructed to allow the angle between the laser beam and the resonator to be changed continuously. The goal is to study the dispersive character of the propagation of light near the infrared resonance involved in the Raman process and to determine whether such dispersion leads to tuning of the coherent Raman emission.

Progress:

Initial experiments with the external resonator conform to theory. Theoretical studies indicate that infrared transitions which are simul-

taneously Raman active could provide a mechanism for tuning the Raman emission. Tuning over a 50 Å range has been observed for low level (i.e., non-stimulated) emission from the crystal $LiNbO_3$, and threshold calculations indicate that the observation of tunable stimulated emission can be expected under reasonable experimental conditions.

Reference Publications and Presentations:

1. R. H. Pantell and R. L. Kohn, "Mode Coupling in a Ruby Laser," IEEE J. Quant. Elect. QE-2 (8) 306-310 (Aug. 1966).

2. P. W. Pheneger and R. H. Pantell, "Quenching Effects in Coupled Lasers," IEEE J. Quant. Elect. QE-2 (9) 644-648 (Sept. 1966).

3. R. H. Pantell, B. G. Huth, H. E. Puthoff, R. L. Kohn, "Mode Coupling in an External Raman Resonator," Appl. Phys. Lett. 9 (3) 104-106 (Aug. 1966).

4. B. G. Huth, N. V. Karlov, R. H. Pantell, H. E. Puthoff, "Elimination of the Effects of Self-Focusing in the Study of the Stimulated Raman Effect by Means of an Off-Axis Resonator System," Microwave Laboratory Report No. 1445, Stanford University (June 1966); submitted to Appl. Phys. Lett.

5. B. G. Huth, N. V. Karlov, R. H. Pantell, "A Quantitative Study of the Stimulated Raman Effect Using an Off-Axis Resonator," IEEE J. Quant. Elect. QE-2 (12) 763-769 (Dec. 1966).

6. R. H. Pantell, F. Pradere, J. Hanus, M. Schott, and H. Puthoff, "Theoretical and Experimental Values for Two, Three and Four Photon Absorption," J. Chem. Phys. 46, 3507-3511 (May 1967).

7. W. R. Callen, B. G. Huth, and R. H. Pantell, "Optical Patterns of Thermally Self-Defocused Light," Appl. Phys. Lett. 11, 103-105 (Aug. 1967).

8. H. E. Puthoff, R. H. Pantell, B. G. Huth, and M. A. Chacon, "Near-Forward Raman Scattering in $LiNbO_3$," Microwave Laboratory Report No. 1529, Stanford University (Apr. 1967); submitted to Phys. Lett.

9. P. W. Pheneger and R. H. Pantell, "Coupled Optical Oscillators," Microwave Laboratory Report No. 1544, Stanford University (May 1967); presented at Sixth International Conference on Microwave and Optical Generation and Amplification, Cambridge, England (Sept. 1966).

10. R. H. Pantell, B. G. Huth, and H. E. Puthoff, "Generation of Non-Threshold Second-Stokes Using an Off-Axis Resonator," Microwave Laboratory Report No. 1551, Stanford University (June 1967), submitted to Appl. Phys. Lett.

11. R. H. Pantell and J. Warszawski, "Laser Power Stabilization by Means of Nonlinear Absorption," Microwave Laboratory Report No. 1564, Stanford University (July 1967); submitted to Appl. Phys. Lett.

12. P. W. Pheneger and R. H. Pantell, "Quenching Effects in Coupled Lasers," IEEE J. Quant. Elect. QE-2 (9) 644-648 (Sept. 1966).

24. PHYSICS AND CHEMISTRY OF OXIDES AND OXIDE SURFACES

G. A. Parks, Associate Professor, Mineral Engineering

Graduate Students:

A. Ahmed
S. Akhtar
R. W. Luce
T E. Paces
C-S. Shi
R. W. Smith
R. L. Burns

Agency Support:

AEC AT(04-3)326-PA3
NSF GF 172
ARPA SD-87

Research Report:

(1) Surfaces of Complex Oxides in Aqueous Systems

Graduate Student: R. W. Luce

Technical Objective:

To relate the surface charge of a solid complex-oxide to the mechanisms and extent of the solid's dissolution in water.

Approach:

The dissolution of the magnesium silicates, serpentine ($Mg_3Si_2O_5(OH)_4$), forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$) is being studied by monitoring the pH and composition of the solution through time. This is done for varied initial conditions for the solid and the solution. The sign and relative magnitude of the surface charge is to be measured by microelectrophoresis as dissolution proceeds. The chemical mechanism of dissolution, derived from the reaction kinetics and surface charge, is being related to the structure of the three solids.

Status Report:

Synthetic and natural crystals have been prepared and characterized

by X-ray diffraction and IR absorption. Twelve month dissolution studies on serpentine have yielded data which allowed calculation of standard free energy of formation values which compare favorably with solution calorimetry data of others. Preliminary kinetics experiments on the serpentine-water system have shown that the exchange of H^+ from solution for Mg^{++} in the crystal can be explained by a mass action effect. However, the adsorption of H^+ and release of H_4SiO_4 from the crystal appears to be related to the surface charge.

(2) Surface of Alumina in Aqueous Systems

Graduate Students: T. E. Paces
R. W. Smith

Technical Objective:

Understanding of the origin of surface charge on Al_2O_3 and its hydrates (e.g., $\alpha Al(OH)_3$, $\alpha AlOOH$) present as solids in aqueous suspension. Clarification of the concept of isolectric points for solids. Ultimately, understanding of the origin of charge on any oxide material in aqueous suspension.

Status Report:

The sign of charge observed is primarily pH dependent. Its magnitude and the pH at which charge is zero are highly sensitive to sample history. Earlier work by G. K. Korpi was thought to show that these differences were not due to differing composition among Al_2O_3, AlOOH and $Al(OH)_3$. His work involved measurement of hydrogen in adsorption by observing pH shifts accompanying immersion of dry solids in aqueous solutions. Correction for effects due to dissolution have been found in error. T. E. Paces is repeating critical parts of Korpi's work, adding analysis of solution for total dissolved aluminum with the intention of making more rigorous corrections and re-working Korpi's results.

If the solubilities of the oxides in question are higher than expected by Korpi, the concentrations of Al(111) hydroxo-complexes produced by dissolution are also higher. It is conceivable that these

species play important change determining roles. R. W. Smith, in co-operation with John Hem of the U.S.G.S. is involved in study of the composition and stability of Al(111) hydroxo-complexes and their adsorption into solids.

(3) Surface Conductivity and Contact Charge Transfer by Insulating Oxides

Graduate Students: A. Ahmed
C-S. Shi

Technical Objective:

Identification of charge carriers responsible for surface conductivity of insulating oxides in the presence of water vapor and understanding of temperature and humidity dependence of conductivity and oxide/oxide contact charge transfer.

Status Report:

Earlier work by J. H. Anderson demonstrated (with some reservation) that hydrogen ions (probably hydrated) are the predominant carriers in the SiO_2 - H_2O (gas) system above 20% relative humidity at 25°C. Serious polarization problems plagued his D.C. conductivity measurements. Mr. Shi has demonstrated that electrodes reversible to hydrogen ion ("black platimun") polarize very little. He is now involved in confirming Anderson's results.

Hydrogen ion donors on oxide surfaces are probably of two types, metal-hydroxide groups and adsorbed water molecules. In either case the acidity of the metal-hydroxide group should modify donor ionization energy, carrier mobility, and oxide-oxide charge transfer. Earlier work (by J. N. Roco) has demonstrated that useful measurements of charge transferred from a ceramic cube to a single sphere of a different oxide could be made. Mr. Ahmed has refined the technique to permit reliable humidity and temperature control and is engaged in studying the reproducibility of measurements and in establishing a tribo-electric series among SiO_2, αAl_2O_3, MgO and ZrO_2.

(4) Simple Paramagnetic Oxide Minerals

Graduate Student: S. Akhtar

Technical Objective:

To determine the paramagnetic susceptibility and magnetic moment of Fe(11) in oxygen co-ordinated synthetic and natural minerals. To evaluate the effect of crystal fields upon the magnetic moment of Fe(11) in sites of cubic, tetragonal, trigonal, orthothombic and monoclinic symmetry.

Approach:

Measure (using Faraday method) the susceptibility of inorganic compounds and minerals with Fe(11) at sites of selected point group symmetry and compare the observed magnetic moments with theoretical moments derived from crystal field theory.

Status Report:

Measurements on Fe(11) doped MgO (octahedra point group) give a magnetic moment of 4.0 Bohr Magneton, which is equivalent to a spin orbit coupling parameter of 80 cm^{-1}. The reduction in spin orbit coupling parameter (free ion $\lambda = 100\ cm^{-1}$) is comparable to that published for Cr^{+++} in MgO (28%) and Ni^{++} in Tutton salt (17%).

Measurements and crystal field calculations for other selected compounds are in progress.

(5) Fragmentation Modes in Brittle Solids

Graduate Student: R. L. Burns

The purpose of this project was originally to study the relation between projectile momentum and geometry on fracture behavior of brittle solids broken by impact and the size distribution of resulting fragments. Early literature study revealed inconsistency in the relationships between crystal structure and the system of cleavage planes resulting from fracture for the specimen system - α quartz. Burns has proposed that the

α - β transformation temperature is sufficiently decreased at crack tips due to high local stress, that the transformation occurs in a zone or halo around the crack tip. Thus fracture occurs in β quartz. This hypothesis is supported by the observation that the system of cleavage planes produced in fracture of quartz is rational in the β quartz structure but not in the structure of α quartz. An optical anomaly at the crack tip is being analyzed to ascertain whether or not it is evidence of the presence of local transformation.

25. THERMODYNAMICS AND KINETICS OF GAS-METAL REACTIONS

N. A. D. Parlee, Professor, Department of Mineral Engineering

Research Associate:

H. D. Kunze

Graduate Students:

R. N. Anderson
P. J. Depuydt
M. M. A. El-Naggar
N. M. El-Tayeb
J. Gani
W. H. Goodnow
J. Lee
E. M. Sacris
I. D. Shah
M. C. Speer
M. T. Utine
L. R. Velho

Agency Support:

NSF GP 1135
ARPA SD-87

Technical Objective:

To study the equilibria and the rates of important simple gas-metal reactions and interactions in order to elucidate the thermodynamics and the kinetic mechanisms involved.

Approach:

Determination of thermodynamic and kinetic relations from equilibrated and dynamic systems of gases and liquid metals. The gases include (in addition to H_2 O_2 N) low boiling metal species such as Ca and Mg.

Research Report:

(1) Graduate Student: I. D. Shah

A new type of gas-liquid unsteady-state diffusion cell originated

by Parlee and associates was refined by Shah[1] and used to redetermine the Arrhenius equation for D_{oxygen} in liquid silver with improved precision. His main effort involved measuring D_{oxygen} in liquid Ag-Au, Ag-Pt and Ag-Pd alloys[2] up to concentrations of 25 to 50 percent of these alloying elements. The solubilities and thermodynamics of oxygen in these alloys were also established by him[2,3] using an improved technique -- this data being required to calculate diffusion coefficients. Thermodynamic work on the more complex Ag-Cu-O system was done here by Sacris.[4] Some of this work has been published and the remainder is in process of publication. A solid ZrO_2 (CaO) cell technique is being developed by Mr. El-Naggar in the laboratory for measuring diffusion coefficients of oxygen in more oxygen-avid liquid metals.

(2) Graduate Student: E. M. Sacris

Methods for studying the diffusion of hydrogen and nitrogen and measuring D_H and D_N in liquid iron developed by El-Tayeb[5,6,7] in this laboratory are being adapted for hydrogen in liquid copper, nickel and other metals. These unsteady state methods are providing the scientific literature with the first diffusion coefficients of hydrogen in liquid metals. The activation energy of diffusion for hydrogen appears to be the same in solid and liquid iron. If this turns out to be the case for other liquid metals it should throw considerable light on the mechanism of diffusion in such systems.

(3) Graduate Students: J. Gani
L. R. Velho

Graduate students El-Tayeb, Goodnow, and Shah, in this laboratory developed the mathematical model of the first known successful steady-state gas liquid metal diffusion cell. Velho has applied the cell to the Ag-O system in the laboratory and has demonstrated[8,9] that the diffusion coefficients of oxygen in liquid silver obtained by this method are the same as found by the well established unsteady-state technique. He has also found a method by which the cell, by operating first unsteady and later steady can be used to measure solubilities[9] and diffusivities

simultaneously. This could be very valuable for gases whose solubilities in liquid metals are too small to measure with accuracy by conventional methods. Gani is continuing with this work but with another gas-liquid metal system.

(4) Graduate Students: J. Lee
M. T. Utine
L. R. Velho

Former graduate student Zoellner demonstrated by a kinetic application of a Sieverts apparatus that the rate of absorption of oxygen in induction stirred liquid silver can be described by a model involving diffusion control through a thin "surface boundary layer" or "high concentration gradient layer." The activation energy was approximately the same as that of diffusion of oxygen in silver. Utine,[10] using a similar technique has demonstrated that the rate of effusion (non-bubble forming evolution) of oxygen from induction stirred liquid Ag can be described by a model completely analogous to that for absorption, that the rate constants for both processes are the same at constant T, and that the activation energy of the processes are essentially the same as for diffusion of oxygen in silver. These mechanism-models apply over considerable ranges of stirring rates. Velho is presently "sharpening" the work, but Lee, who has just arrived, will attempt to extend the work to a wide range of stirring rates and study the effects of various surface conditions; up until now the surface has always been that of pure mirror-like silver.

(5) Graduate Student: R. N. Anderson

The Sieverts technique for studying nitrogen-nitride equilibria in liquid iron alloys developed by Parlee and co-workers is being used as the basis for work on hydrogen-hydride and nitrogen-nitride equilibria in liquid uranium alloys. The most fruitful direction at present is with Sn-U alloys, where the thermodynamics of the precipitation of uranium nitrides in these alloys is being developed. Certain kinetic factors are controlling in the work and it is being found necessary to study these more or less simultaneously with the thermodynamics.

(6) Graduate Student: M. C. Speer

The solubilities and thermodynamics of volatile metals, like Ca and Mg, in liquid iron are being investigated. The inert gas transport technique originally tried did not prove successful, hence an entirely different technique and apparatus have been developed. This involved a vertical closed evacuated tubular "bomb" in a two zone furnace with the Mg at the lower fixed temperature (T_1) and the iron or iron-carbon alloy above it at the higher fixed temperature (T_2). This method appears to be successful. An interesting feature is the use of solidified magnesium in the "cold" end of the bomb (well below the liquid Mg) to seal the system during the equilibration.

(7) Post Doctoral Student: Dr. H. D. Kunze

Dr. Kunze and associates have developed a new method of correlating and predicting activity coefficients, activities and solubilities of elements like nitrogen and sulfur in simple and complex liquid alloy systems, which perhaps can be extended to solid alloys. The method of the use of known interaction coefficients in binary alloys to predict activities and solubilities in dilute complex alloys is of course widely known, but this conventional method is only approximate for more concentrated alloys and fails completely at very high concentrations. Dr. Kunze's method does not involve interaction coefficients at all but can be used for very high concentrations and very complex systems. He is presently engaged in remeasuring and measuring nitrogen solubilities in selected iron alloys to more firmly establish and extend the method. Since coming to Stanford he has also shown that the correlations between interaction coefficient (e.g. of nitrogen with alloying elements in liquid iron) and position in the periodic table such as developed by Schenck and others are very crude and that these can be modified to develop ones more reliable and more compatible with the known atomic structure of the alloying elements and with newer theories of liquid metal solutions.

Reference Publications and Presentations:

1. I. D. Shah and N. A. D. Parlee, "The Diffusivity of Oxygen in Liquid Silver," Trans. (Met. Soc.) AIME 239, 763-764 (May 1967).

2. I. D. Shah, "Thermodynamics and Kinetics of Absorption of Oxygen in Stagnant Liquid Silver and Silver Alloys," Stanford University Ph.D. Thesis (June 1967).

3. I. D. Shah and N. A. D. Parlee, "The Solubility of Oxygen in Ag-Au, Ag-Pt, and Ag-Pd Alloys," submitted to Trans. (Met. Soc.) AIME.

4. N. A. D. Parlee and E. M. Sacris, "Oxygen-Oxide Equilibria in Silver-Copper Alloys," accepted for publication Trans. (Met. Soc.) AIME.

5. N. M. El-Tayeb and N. A. D. Parlee, "The Diffusion of Hydrogen in Liquid Iron, Trans. (Met. Soc.) AIME 239, 1345-1351 (Sept. 1967).

6. N. M. El-Tayeb and N. A. D. Parlee, "The Diffusion of Nitrogen in Liquid Iron Alloys," accepted for publication Trans. (Met. Soc.) AIME.

7. N. M. El-Tayeb and N. A. D. Parlee, "The Diffusion of Hydrogen in Liquid Iron-Carbon Alloys," submitted to Trans. (Met. Soc.) AIME.

8. I. D. Shah, L. R. Velho, and N. A. D. Parlee, "Thermodynamics and Kinetics of Oxygen Absorption in Stagnant Liquid Ag, and Ag-Au, Ag-Pd and Ag-Pt Alloys," presented at 1967 Annual Meeting of AIME, Los Angeles.

9. L. R. Velho, N. M. El-Tayeb, W. H. Goodnow, and N. A. D. Parlee, "A Steady-State Gas-Liquid Metal Diffusion Cell," submitted to Trans. (Met. Soc.) AIME.

10. M. T. Utine, "Kinetics of Oxygen Effusion From Induction-Stirred Liquid Silver," Stanford University Dept. of Mineral Engineering M. S. Thesis (June 1967).

26. ELECTRICAL, OPTICAL AND METALLURGICAL PROPERTIES OF SEMICONDUCTING MATERIALS

G. L. Pearson, Professor, Electrical Engineering

Professional Associates:

J. W. Allen
J. M. Baranowski
A. Majerfeld
I. Kuru

Graduate Students:

M. G. Buehler
E. G. Dierschke
V. J. Grande
J. S. Harris, Jr.
M. Ilegems
D. H. Landis
D. H. Loescher
S. F. Nygren
M. Shyam
K. K. Shih
C. H. Ting
A. B. Y. Young

Agency Support:

NASA NsG-555
Army ARO(D)-155
ONR Nonr 225(83) and (59)
ARPA SD-87

Technical Objectives:

To prepare new semiconducting materials, measure their pertinent properties, and construct novel devices therefrom.

Research Report:

(1) The Electrical and Metallurgical Properties of Defects in Compound Semiconductors

Graduate Students: E. G. Dierschke
M. Ilegems
D. H. Landis

"Green Electroluminescence in GaP." The purpose of this project is to study injection electroluminescence at p-n junctions in GaP. The objective is to determine the nature of the recombination processes and to use luminescence as a tool to study other properties of the crystal and to design an efficient green emitter.

"Fundamental Studies on the Properties of the $Ga_xAl_{(1-x)}As$ System." In this project we are investigating the Ga-Al-As ternary system. The phase diagram has been derived from fundamental considerations and single crystals have been grown by a liquid epitaxial method. We are particularly interested in the composition region near the crossover point from direct (GaAs) to indirect (AlAs) band gap material.

"The Effects of Gamma Radiation in Silicon Semiconductor Devices." A new computer technique has been developed to obtain energy levels and introduction rates of defect centers introduced in silicon as a function of Co-60 gamma ray fluence.[7] These measured parameters have been used to predict degradation rates of both majority and minority carrier silicon devices under various radiation environments.

(2) Properties of Compound Semiconductors Under High Electron Fields

Graduate Students: V. J. Grande
J. S. Harris
A. Majerfeld

"Microwave Oscillations in Compound Semiconductors." The purpose of this project is to study the relationship between the energy band structure of semiconducting materials and the generation of coherent microwave oscillations.[10] Measurements are presently being made to determine the effect of uniaxial stress on resistivity and the Gunn effect in GaAs.

"Electrical Properties of $GaAs_xP_{1-x}$ Current Limiters." The purpose of this project is to study the current-voltage characteristics of $GaAs_xP_{(1-x)}$ diodes for x near the crossover from a direct (GaAs) to an indirect (GaP) band gap. These materials are useful for constructing high speed current limiters.[11,13]

"Applications of $GaAs_{0.7}P_{0.3}$ to Microwave Switches." The purpose of this project is to determine the feasibility of utilizing bulk $GaAs_{0.7}P_{0.3}$ material in microwave switch or limiter applications. It is believed that greater microwave average power capability and/or switching speed with respect to present day devices may be realized.

(3) Diffusion in Compound Semiconductors

Graduate Students: J. Baranowski
S. F. Nygren
A. B. Y. Young
C. H. Ting

"Spectra of Transition Metals in Semiconductors." Studies relating the effects of crystal-field splitting to the spectra of the following systems have been carried out:[1,2,9] $Fe(d^6)$ in ZnSe, ZnTe, CdS, CdTe, GaP and GaAs; $Co(d^7)$ in ZnSe, ZnTe, GaP and GaAs; and $Ni(d^8)$ in GaP.

"Properties of Rectifying Junctions in $GaAs_xP_{1-x}$." The purpose of this project is to study the preparation and properties of rectifying junctions in GaP and $GaAs_xP_{(1-x)}$. Crystals have been prepared by both vapor and liquid epitaxy processes. The effects of crystal imperfections are of special interest.

"Donor Impurities in GaP." The shallow donors S, Se and Te are under investigation. The ternary system Ga-P-S has been delineated with particular emphasis on the solubility and diffusion parameters.

"Diffusion of Zn in GaAs." We are presently (1) determining the activation energy of diffusion under isoconcentration conditions, (2) carrying out detailed measurements of diffusion depth versus diffusion time and temperature, and (3) measuring the electrical properties of the diffused layers.

Reference Publications and Presentations:

1. D. H. Loescher, J. W. Allen, and G. L. Pearson, "The Application of Crystal Field Theory to the Electrical Properties of Co Impurities in GaP," J. Phys. Soc. Japan 21, 239 (Supplement 1966).

2. J. M. Baranowski, J. W. Allen, and G. L. Pearson, "Crystal Field Spectra of $3d^n$ Impurities in II-VI and III-V Compound Semiconductors," Phys. Rev. 160, 627 (1967).

3. M. G. Buehler, "A Small Four-Point Probe on Thin Plates: Theory and Experiment," Solid-State Electronics 10, 801 (1967).

4. J. A. Higgins, V. J. Grande, and G. L. Pearson, "Signature of the LSA Mode," IEEE Trans. on Electron Devices, ED-14 (Sept. 1967).

5. K. K. Shih, J. W. Allen, and G. L. Pearson, "Gas Phase Equilibria in the System Ga-As-Zn," J. Phys. Chem. Solids (in publication).

6. K. K. Shih, J. W. Allen, and G. L. Pearson, "Diffusion of Zinc in Gallium Arsenide Under Excess Arsenic Pressure," J. Phys. Chem. Solids (in publication).

7. D. Landis and G. L. Pearson, "Radiation-Induced Defects in Semiconductors: a Measurement Technique and Applications to γ-Irradiated Silicon," Proceedings of Santa Fe Conference on Radiation Effects in Semiconductors (in publication).

8. H. C. Casey, M. B. Panish, and L. L. Chang, "Dependence of the Diffusion Coefficient on the Fermi Level: Zinc in Gallium Arsenide," Phys. Rev. 162, 660 (1967).

9. J. M. Baranowski, J. W. Allen, and G. L. Pearson, "The Adsorption Spectra of Nickel in Gallium Phosphide," Phys. Rev. (submitted for publication).

10. G. L. Pearson, "Effects of Composition and Uniaxial Stress on Microwave Oscillations in $GaAs_xP_{(1-x)}$ Alloys," 17th Meeting of CITCE, Tokyo, Japan, Sept. 1966.

11. A. Majerfeld and G. L. Pearson, "A High Speed Current Limiting Device from $GaAs_xP_{(1-x)}$," IEEE Electron Devices Research Conference, Santa Barbara, California, June 1967.

12. V. J. Grande, J. A. Higgins, C. F. Quate, and G. L. Pearson, "Observations of the Transition from Gunn Mode to LSA Mode," IEEE Electron Device Research Conference, Santa Barbara, California, June 1967.

13. A disclosure to seek a U. S. Patent on a "High Speed Current Limiting Device from $GaAs_xP_{(1-x)}$" was filed on Sept. 28, 1967 by Stanford University through the Research Corporation. The inventors were G. L. Pearson, J. W. Allen, and A. Majerfeld.

27. SCATTERING OF RADIATION BY LIQUIDS AND POLYMERS

R. Pecora, Assistant Professor, Chemistry

Graduate Student:

J. W. Breslow

Agency Support:

NSF GP 5723

Technical Objective:

To formulate theories of the scattering of radiation from liquids and polymer systems in relation to their structure and thermal motions.

Approach:

Theories of the radiation scattering are first formulated in terms of the relevant fluid correlation functions. Models of the correlation functions for particular types of system are then constructed in terms of the fluid structure and transport parameters.

Research Report:

(1) Polymers

A) A theory of the spectrum of light scattered from dilute polymer solutions in terms of the Van Hove space-time correlation function has been formulated and applied to both the rigid-sphere and random-coil models of polymer structure. Some comments on the theory and suggestions for experiments on pure liquids and mixtures composed of small molecules have also been made.(1)

B) The spectral distribution of light scattered from a dilute monodisperse solution of rigid-rods has been investigated. It is found that the rod's rotational diffusion coefficient affects the spectral width of the scattered light only when the scattering is observed at large angles and the rods are large (2000-3000 Å).(2)

C) The theories described in A and B above apply only to optically isotropic polymers. When the polymers are optically anisotropic an additional scattering of light is found whose spectral width is closely related to molecular rotations. A general theory of this "anisotropic" scattering has been formulated and applied to cases where the translational and anisotropic rotational diffusion equations describe the polymer motions. It is shown that in the case of completely anisotropic rigid molecules, the "anisotropic" scattering spectrum is described by the sum of five Lorentzians.[3]

D) In addition, the intensity and spectral distribution of light scattered by polymers perturbed by periodic external fields has been investigated. It is found that for acoustic fields, the shifted components of the scattered light are too weak to be observed. For external electric fields, the shifted components are probably observable for highly polar polymers - although such experiments would be very difficult.

(2) Liquids of Small Molecules

A) Work is continuing on the theory of the depolarized backgrounds in the scattering from liquids of small molecules. In particular, models of the correlated part of the scattering spectrum are being constructed.

B) A Kubo theory of the dispersion of electric birefringence of liquids composed of optically anisotropic, non-polar molecules has been formulated in terms of generalized space-time correlation functions. It is shown that the formal expressions for the Kerr constant are proportional to the same combination of anisotropy and correlation factors as those for the small-angle, anisotropic light scattering intensity.

Reference Publications and Presentations:

1. R. Pecora, "Fine Structure of Rayleigh Scattered Light," in Electromagnetic Scattering (R. L. Rowell and R. S. Stein (Eds.), Gordon and Breach, New York, 1967).

2. R. Pecora, "Spectral Distribution of Light Scattered from Monodisperse Rigid Rods," (to be submitted for publication).

3. R. Pecora, "Spectrum of Light Scattered From Optically Anisotropic Macromolecules," (Paper to be presented at the American Chemical Society Polymer Symposium, San Francisco, April, 1968).

28. PHASE TRANSITION KINETICS

G. M. Pound, Professor, Materials Science

Graduate Students:

R. E. Apple
A. I. Michaels
Y. Miyazawa
K. Nishioka

Agency Support:

AFOSR-1283-67
NBS CST-388

Technical Objective:

To gain a better understanding of the physics of phase transformations and other thermally activated rate processes of interest in materials science, metallurgy, mechanical engineering, and meteorology.

Approach:

Theoretical and experimental investigations of homogeneous nucleation in condensation from the vapor and freezing of liquids, of heterogeneous nucleation on substrates and of other thermally activated rate processes.

Research Report:

(1) Effective Surface Free Energy of Small Clusters

Graduate Student: A. I. Michaels

A modification of the Band method for estimating the effective surface free energy of small clusters from vapor density data is being used in conjunction with the Lothe-Pound theory of homogeneous nucleation to predict supersaturations required for appreciable homogeneous nucleation rate in condensation. A new feature of the present method is that the rotational partition function of the cluster is being considered. This complicates the problem such that an electronic computer must be used in performing the calculations.

(2) The Entropy of Small Systems

A normal coordinate analysis is being used to calculate the entropy that a small system does not have because it is not a part of a bulk phase. This reduction in entropy comes about because certain vibrations of wave length longer than the dimensions of the small system can be operative only in the bulk phase. The result is important in nucleation theory and is known as the replacement factor.

(3) Homogeneous Nucleation in Freezing

Graduate Student: Y. Miyazawa

It has been shown that the replacement factor for homogeneous nucleation in the condensation of liquid from vapor may be obtained from experimental data on the homogeneous nucleation of crystals from liquid. In this work the Turnbull techniques for measuring the rate of homogeneous nucleation in freezing of dispersions of small droplets are being applied to a variety of liquids such as H_2O, C_6H_6, etc. The replacement factor, i.e. the partition function for the six degrees of freedom for motion of the crystallite nucleus as a whole in the bulk liquid, will be obtained from the kinetic coefficient of the experimental nucleation rate equation.

(4) Heterogeneous Nucleation on Substrates by Field Emission Microscopy

Graduate Student: R. E. Apple

The critical ad-population for nucleation of silver crystallites on tungsten field-emitter tips in 0.09 monolayers. This nucleation is of the "island" type. However the crystallites of a number of other metals (e.g. Au, Cd, Ni, Zn) arise from a multilayer adsorbate on the tip surface. The treatment and description of this latter nucleation process are difficult, because the chemical potential of the adsorbate is as yet undetermined. In this work an attempt is being made to determine this chemical potential at nucleation by measuring the thermal beam flux necessary for a constant adatom population. Tellurium, bismuth and carbon tetrachloride are being used as adsorbates. It is hoped to delineate the conditions for the two respective mechanisms noted above.

(5) Dislocation Dynamics

Graduate Student: K. Nishioka (with Professor W. D. Nix)

All treatments of the motion of jogged dislocations under shearing stresses involve some idealization in regard to jog spacing along dislocation lines. Actually, the spacing and density of jogs should vary both with position and time for either thermal jog formation or intersection jog formation. In order to remove this difficulty in the theory, a dynamic, statistical treatment of the actual jog distribution is being carried out.

Reference Publications:

1. K. Sigsbee and G. M. Pound, "Heterogeneous Nucleation from the Vapor," Advances in Colloid and Interface Science, 1 (3) 335-390 (Aug. 1967).

2. H. Karge, H. Heyer, and G. M. Pound, "Die spezifische Freie Oberflächenenergie von Kristallen als Funktion der temperatur," Zeit, für physikalische Chemie Neue Folge 53, 1-6, 294 (1967).

3. R. Lacmann and G. M Pound, "Die Gleichgewichtsform von Mischkristallen," Zeit, fur physikalische Chemie Neue Folge 53, 1-6, 143 (1967).

4. J. Lothe and G. M. Pound, "The Concentration of Clusters in Nucleation and the Classical Phase Integral," J. Chem. Phys. (in press).

5. F. F. Abraham and G. M. Pound, "A Reexamination of Homogeneous Nucleation; Statistical Thermodynamic Aspects," J. Chem. Phys. (submitted).

6. F. F. Abraham and G. M. Pound, "Free Energy of Formation of Droplets from Vapor and Dependence of Surface Tension on Radius," J. Chem. Phys. (submitted).

7. R. D. Gretz and G. M. Pound, "Nucleation of Crystals in Multilayer Metallic Adsorbates," J. Appl. Phys. Lett. (in press).

8. J. Lothe and G. M. Pound, "Statistical Mechanics of Nucleation," Chapter for book on Nucleation, ed. A. C. Zettlemoyer, Elsevier, Amsterdam (in press).

29. SOLID STATE OSCILLATION

C. F. Quate, Professor, Applied Physics and Electrical Engineering

Graduate Students:

D. E. Caddes
R. D. Earhart
J. F. Havlice
W. H. Haydl
D. J. Jefferies
J. E. Murray
B. A. Richardson
R. B. Thompson
C. D. Wilkinson

Agency Support:

ONR Nonr 225(48)
AF 30(602)-3595
AF 33(615)-3670
AF 49(638)-1429
NASA Ngr-05-020-165

Research Report:

(1) Electroacoustic Amplifiers

Graduate Student: D. J. Jefferies

The primary purpose of this program is to produce operational acoustic amplifiers in the frequency range 1 - 10 GHz. In piezoelectric semiconductors, sound amplification occurs when the charge carriers are drifted faster than the sound velocity. We have observed acoustic gain in single crystals of semiconducting cadmium sulphide at frequencies up to 2.4 GHz; the magnitude of the observed gain is in reasonable agreement with theoretical predictions. We have also observed spontaneous acoustic noise generation between 0.5 and 5.0 GHz from an amplifier operating in the non-linear region. This noise is generated by amplification of the thermal sound waves in the crystal.

We are also interested in other possible mechanisms for obtaining acoustic gain. Semiconducting strontium titanate is electrostrictive above a phase transition at 11°K; it appears that the properties of this

crystal are ideal for obtaining a carrier-acousticwave interaction through electrostrictive coupling at temperatures just above the transition. We have prepared samples of reduced strontium titanate with the optimum resistivity, and have investigated the current-voltage characteristic around the phase transition. Below the transition, the crystal is piezoelectric and we observe current saturation similar to the type seen in cadmium sulphide, due to the acousto-electric effect. Above the transition, we have not been able to apply sufficiently high fields to the crystal to reach saturation, since carrier ionization sets in. We are working on other methods of doping the crystal in order to avoid this problem.

(2) Finite Amplitude Acoustic Waves in Crystalline Solids

Graduate Students: B. A. Richardson
R. B. Thompson
C. D. Wilkinson

Our objective in this project is to study the behavior of acoustic waves of large amplitude in crystalline solids, in particular the manner in which this behavior deviates from that predicted by the small signal formulation of elasticity. We have used the technique of Bragg diffraction to monitor the spatial growth of the various acoustic harmonics of a wave as it propagates through a crystal. This technique enables us to distinguish bulk nonlinear effects occuring within the crystal from surface effects.

Three crystals were studied, SiO_2, MgO, and MnF_2. The effects observed include the following: valuation of the attenuation of the fundamental with input power level, the presence of first through fifth harmonics, and the growth and decay of these harmonics as a function of distance propagated by the acoustic pulse. We have been able to obtain quantitative agreement with theoretical predictions and thereby estimate the relevant third-order elastic constants.

Reference Publications:

1. W. H. Haydl and C. F. Quate," Current Oscillations in Piezoelectric Semiconductors - Part I, and Part II," Microwave Laboratory Report No. 1446, Stanford University (June 1966); to be published in J. Appl. Phys.

2. B. A. Auld, C. F. Quate, H. J. Shaw, and D. K. Winslow, "Acoustic Quarter Wave Plates at Microwave Frequencies," Appl. Phys. Lett. 9, 436-438 (Dec. 1966).

3. E. G. H. Lean, C. F. Quate, and H. J. Shaw, "Continuous Deflection of Laser Beams," Appl. Phys. Lett. 10, 48-51 (Jan. 1967).

4. C. F. Quate, "Optical Amplification with a Low Frequency Pump," Microwave Laboratory Report No. 1504, Stanford University (Jan. 1967).

5. W. H. Haydl, "High Field Domains in n-Type Cadmium Sulphide," Appl. Phys. Lett. 10 (2) 36-38 (Jan. 1967).

6. M. H. Jorgensen, N. I. Meyer, and C. F. Quate," Amplification of Sound in Crystals with Strong Current Striction and Elasto-Conductivity Effects," Sol. State Comm. 5 (7) 559-561 (1967).

30. MICRO-MECHANISMS OF DEFORMATION AND RELATED THERMALLY ACTIVATED PROCESSES IN CEMENT AND CONCRETE

C. W. Richards, Associate Professor. Civil Engineering

Graduate Students:

W. H. Bray
F. Radjy
E. J. Sellevold

Agency Support:

ARPA SD-87

Technical Objectives:

To investigate the internal structure and micro-mechanisms of deformation of hardened portland cement paste and concrete.

To determine the interaction of water (in its various states) with the solid phase in the deformation process. To study the relations between structure and properties of the material, with a view toward improving properties through alterations in structure.

Approach:

Application of thermodynamic, kinetic, and mechanical principles through the study of a) internal friction, b) anelastic creep, and c) diffusion and adsorption. Experimental measurements include dynamic modulus and loss tangent, recoverable creep diffusion coefficients, and adsorption isotherms, all as functions of time (or frequency) temperature, and moisture content. Supporting work includes studies of the hydration process and the occurrence of phase transitions, through differential thermal analysis, thermogravimetric analysis, etc.

Research Report:

a) Internal friction: Two modulus transitions have been studied, one at 0°C and one at -90°C. On the basis of a thermodynamic analysis we associate these transitions with changes of state in the water involving

transfers of material between phases. The strength of each transition is related to the quantity of water present: capillary water in the case of the 0°C transition, and adsorbed (gel) water in the case of the -90°C transition. The method may provide a convenient means of measuring these quantities, because of their high degree of reproducibility.

b) Apparatus for measuring creep recovered after removal of load has been constructed. With this apparatus it will be possible to measure anelastic creep curves starting at a few milliseconds. The resulting curves will be analyzed in terms of viscoelastic response spectra.

c) Diffusion apparatus has been constructed and will be in operation shortly. Extensive adsorption and desorption data have been accumulated for room temperature-cured specimens and specimens cured in steam at atmospheric pressure. The improved stability of the latter specimens makes them particularly useful in measuring high temperature effects.

A thermodynamic analysis of creep and shrinkage has been carried out, resulting in a further refinement of Powers' model for these phenomena.

Reference Presentation:

C. W. Richards, "Internal Friction in Cement Paste at Low Temperatures," informal presentation at the Fourth Conference on the Matrix of Concrete, University of Illinois, Sept. 1967.

31. SPECTROSCOPY AND QUANTUM ELECTRONICS

A. L. Schawlow, Professor, Physics

Professional Associates:

R. M. Macfarlane
M. J. Weber
R. M. White

Graduate Students:

M. J. Berggren
J. L. Emmett
R. L. Greene
J. F. Holzrichter
S. A. Johnson
B. McCaul
E. D. Nelson
J. C. Nickerson, III
J. L. Rapier
D. D. Sell
S. E. Stokowski
W. B. Tiffany
J. Y-m. Wong

Agency Support

Army DA 31-124-ARO-D-208
ONR Nonr 225(48) and (78)
NASA NsG 331
NASA Ngr 05-020-166
ARPA SD-87

Technical Objective:

To study the interaction between electromagnetic radiation and matter, to extend the range of coherent light techniques, to apply coherent and conventional light to elucidate problems in the physics of solid materials.

Approach:

High-resolution spectroscopy and fast-pulse electro-optical systems, using lasers where appropriate.

Research Report:

(1) Optical Transition Probabilities

Graduate Student: S. E. Stokowski

A study of optical transition probabilities between electronic levels of ions in crystals, and of the ways in which they are modified by the crystalline surroundings, lattice vibrations and applied electric fields. The spectrum of Cr^{3+} in $SrTiO_3$ is being studied. Theoretical studies are being made of spectra of ions in crystals.

(2) Far Infrared Spectra of Crystals

Graduate Students: M. J. Berggren
J. Y-m. Wong

A far infrared spectrometer has been applied to studies of spectra of crystals in the wavelength region from 60 to 1200 microns. The spectra of Ti^{3+} and V^{4+} ions in Al_2O_3 and of Fe^{2+} ions in MgO have been studied experimentally and theoretically. These spectra are some of the few cases in which the dynamic Jahn-Teller effect is important and can be studied quantitatively.

Another study concerns ion pair systems possessing large exchange couplings, as would be characteristic of the first, second, third, and fourth nearest neighbor schemes. Preliminary data indicate the existence of several such systems, although their identification is as yet uncertain.

Microwave resonances for fourth-neighbor chromium pairs in ruby have been observed optically. It is expected that the measurements will give the splittings of the S=3 ground state of these ferromagnetically coupled pairs.

(3) Optical Maser Research

Graduate Student: S. A. Johnson

Attention is directed to the search for strong, sharp lines in a crystal for wavelength standards, and to the factors controlling line widths. A study of line widths and positions in $LaF_3:Nd^{3+}$ has been completed.

We have measured the temperature dependence of the linewidths and positions for a number of transitions in the spectrum of $LaF_3:Nd^{3+}$. As the temperature increases, all lines broaden because of relaxation and Raman scattering of phonons. Relative to the ground state, all

observed levels shift to lower energies as the temperature increases. Most lines show the usual shifts to the red. All these effects are qualitatively attributable to lattice vibrations. In general, the level shifts increase for the higher levels so that, ordinarily, line shifts are to the red with increasing temperatures. However, because of irregularities of the magnitudes of the level shifts, a few lines show shifts to the blue with increasing temperature, over some temperature ranges.

(4) Energy Transfer in Solids

Graduate Students: J. L. Emmett
J. Holzrichter
S. A. Johnson

The purpose is to study methods of exciting solid materials for visible, and possibly ultraviolet, maser action, and to investigate energy transfer processes between energy levels and between ions. Spectroscopic studies of energy transfer are continuing. New spectrographic techniques using an image orthicon camera are being investigated, and are nearly ready to use. A high power flash source for ultraviolet pumping has been constructed.

(5) Spectroscopic Studies in Infrared and Optical Quantum Electronics

Graduate Students: J. L. Emmett
E. D. Nelson
J. L. Rapier
D. D. Sell
W. B. Tiffany

The purpose is to use lasers as tools for basic studies of the interaction of light and matter. It is also desired to use spectroscopic and other studies of the interaction between light and matter. Particular emphasis is given to understanding the properties of solid state laser materials, and the requirements for exciting them. The studies also include design of a solid state laser, tunable over a narrow range, for chemical catalysis studies.

The gas-phase photochemical addition of bromine to olefin molecules

has been studied by inducing the reaction with monochromatic light near 6940 Å from a pulsed, tunable ruby laser. The use of this technique has led to the observation and elucidation of a new phenomenon in the photochemistry of bromine, and has yielded new information on certain molecular energy transfer processes. It is found that at this wavelength the reaction proceeds by means of free radical chains, as at shorter wavelengths. With light of wavelength shorter than 6800 Å, the Br atoms responsible for these chains are known to result from direct dissociation of Br_2 molecules upon absorbing light in the continuum. By contrast, at 6940 Å direct dissociation is shown to be negligible. Instead, the Br_2 molecules are excited to individual bound levels 500 to 800 cm^{-1} below the required dissociation energy. Additional energy is furnished by subsequent collisions, so that about one percent of the excited molecules become dissociated. The rest relax by collisions to the ground state at a rate of somewhat higher than the gas-kinetic collision rate.

(6) Spectroscopic Studies of Magnetic Materials

Graduate Students: R. L. Greene
D. D. Sell

This study was undertaken to investigate the effect of magnetic interactions on the optical spectra of ordered magnetic materials. The first observation of sharp line fluorescence in antiferromagnetic manganese fluoride (MnF_2) is reported and two new phenomena associated with this fluorescence are identified. It is shown that the major portion of the fluorescence results from the radiative decay of localized excitons. Localized excitons have been previously identified in the spectra of molecular crystals and semiconductors. The first quantitative evidence for their importance in the spectra of magnetic insulators is presented here. It is also shown that certain transitions in the fluorescence spectrum of MnF_2 correspond to the de-excitation of an excited manganese ion combined with the creation of a spin wave. Such transitions are called spin wave sidebands in analogy with the more familiar vibrational (phonon) sidebands.

Reference Publications:

1. S. E. Stokowski, S. A. Johnson, and P. L. Scott, "Vibronic Transitions in Ruby and MgO:V^{2+}," Phys. Rev. 147 (2) 544-546 (July 1966).

2. J. P. Markiewicz and J. L. Emmett, "Design of Flashlamp Driving Circuits," J. Quant. Elect. QE-2 (11) 707-711 (Nov. 1966).

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4. R. M. Macfarlane, "Stress Induced Trigonal Crystal-Field Parameters in Some Oxide Lattices," Phys. Rev. 158 (2) 252-255 (June 1967).

5. D. D. Sell, R. L. Greene, and R. M. White, "Optical Exciton-Magnon Absorption in MnF_2," Phys. Rev. 158 (2) 489 (June 1967).

6. E. D. Nelson and J. Y. Wong, "Spectral Purity for Far Infrared Grating Spectroscopy," Applied Optics 6 (7) 1259-1266 (July 1967).

7. R. M. Macfarlane, "Zero Field Splittings of t_2^3 Cubic Terms," J. Chem. Phys. 47, 2066 (1967).

8. W. B. Tiffany, "Repetitively Pulsed, Tunable Ruby Laser with Solid Etalon Mode Control," to be published, Appl. Opt. (July 1967).

9. R. M. Macfarlane, J. Y. Wong, and M. D. Sturge, "Dynamic Jahn-Teller Effect in Octahedrally Coordinated d^1 Impurity Systems," submitted to Phys. Rev.

10. J. Y. Wong, "Far Infrared Spectra of Iron-doped MgO," submitted to J. Chem. Phys.

11. W. B. Tiffany, "Selective Photochemistry and Molecular Dynamics of Bromine Using a Ruby Laser," submitted to J. Chem. Phys.

12. J. L. Emmett, "Transverse Stimulated Emission in Liquids," submitted to Phys. Rev.

13. A. L. Schawlow and H. G. Freie, "Lasers," in Advanced Optical Techniques, A.C.S. van Heel, editor, North Holland Publishing Company (1967).

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15. J. Y. Wong, M. J. Berggren, and A. L. Schawlow, "Far Infrared Spectra of V^{4+} and Co^{2+} Single Ions in Corundum," Proceedings of Conference on Optical Properties of Ions in Crystals, Sept. 1966.

16. E. D. Nelson, J. Y. Wong, and A. L. Schawlow, "Far Infrared Spectra of $Al_2O_3:Cr^{3+}$ and $Al_2O_3:Ti^{3+}$," Phys. Rev. 156 (2) 298-308 (Apr. 1967).

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19. J. L. Rapier, A. L. Schawlow, and H. H. Heimple, "Spontaneous Emission from a Helium-Neon Laser as a Convenient Wavelength Standard," submitted to Am. J. Phys.

20. W. B. Tiffany, H. W. Moos, and A. L. Schawlow, "Selective Laser Photocatalysis of Bromine Reactions," Science 157 (3784) 40-43 (July 1967).

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32. INTERACTIONS OF ELECTROMAGNETIC AND ACOUSTIC RADIATION WITH SOLIDS

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Agency Support:

AF 30(602)-3595
AF 19(638)-5545
AF 33(615)-3670
AF 49(638)-1429
ONR Nonr 225(48)

Reference Publications:

1. D. K. Winslow and H. J. Shaw, "Multiple Film Microwave Acoustic Transducers," 1966 IEEE International Convention Record Part 5.

2. E. G. H. Lean and H. J. Shaw, "Efficient Microwave Shear-Wave Generation by Mode Conversion," Appl. Phys. Lett. 9 (10) 372-374 (Nov. 1966).

3. B. A. Auld, C. F. Quate, H. J. Shaw, and D. K. Winslow, "Acoustic Quarter Wave Plates at Microwave Frequencies," Appl. Phys. Lett. 9, 436-438 (Dec. 1966).

4. E. G. H. Lean, C. F. Quate, and H. J. Shaw, "Continuous Deflection of Laser Beams," Appl. Phys. Lett. 10, 48-51 (Jan. 1967).

5. W. F. Egan, H. J. Shaw, and M. Chodorow, "Propagation and Variable Delay on a Periodic Circuit of YIG Spheres," J. Appl. Phys. 38 (3) 1230-1231 (Mar. 1967).

6. E. K. Kirchner, H. J. Shaw, and D. K. Winslow, "Experimental Investigation of Saturation Effects in Ferrite Frequency Doublers," IEEE Trans. Magnetics (Dec. 1966).

7. A. Karp, H. J. Shaw, and D. K. Winslow, "Circuit Properties of Microwave Dielectric Resonators," Microwave Laboratory Report No. 1532, Stanford University (May 1967); submitted to J. Appl. Phys.

8. R. M. Malbon, F. Schulenburg, and D. K. Winslow, "Thickness Monitor for Dielectric Films Using a Laser Beam," Microwave Laboratory Report No. 1432, Stanford University (Sept. 1966); submitted to Rev. Sci. Instr.

9. R. M. Malbon, D. J. Walsh, and D. K. Winslow, "Zinc-Oxide Film Microwave Acoustic Transducers," Appl. Phys. Lett. 10 (1) 9-10 (Jan. 1967).

33. CATHODIC PROTECTION AND HYDROGEN EMBRITTLEMENT OF STEEL

O. C. Shepard, Professor, Materials Science

Graduate Student:

M. V. Robertson

Agency Support:

NSF - Research Participation Programs
ARPA SD-87

Technical Objective:

To investigate the fracture of steel when subjected to stress and aqueous corrosion, particularly with regard to hydrogen indroduced into the steel by means of the corrosion reactions.

Approach:

Steel specimens are subjected to corrosion in salt water and to elastic stress. The amount of hydrogen introduced into the steel and the time to rupture are measured.

Research Report:

It was found that hardened 4130 steel will fail under elastic stress when subjected to aqueous corrosion under conditions causing the introduction of hydrogen. Cathodic protection of the steel by more active metals caused earlier failure of the steel. It was also found that low carbon steel will fail under the above conditions when a notch is present so that the steel can be subjected to high elastic stress.

Further work is being conducted to study the mechanisms of the corrosion stress-rupture process and to delineate safe and unsafe conditions.

34. MECHANICAL BEHAVIOR OF SOLIDS

O. D. Sherby, Professor, Materials Science

Research Associates:

Y. Adda
V. Efremov
D. Francois
R. H. Johnson

Graduate Students:

P. M. Burke
W. R. Cannon
D. G. Folgner
A. M. Gaylord
M. R. Gaylord
M. J. Harrigan
J. R. Hauber
I. C. Huseby
Y. E Imbert
A. R McIlree
M. D. Merz
J. W. Moberly
C. M. Packer
J. S. Perrin
J. Readio
S. L. Robinson

Agency Support:

AF 33(615)5374
NASA Ngr-05-020-084
NONR 225(60)
AEC AT(04-3)-326-PA 12
ARPA SD-87
N14-67-A0112-0021

Research Report:

(1) Role of Diffusion in Creep and Stress-Rupture in Solids

(with J. C. Shyne, Associate Professor, Materials Science)

Graduate Students: J. R. Hauber
J. C. Huseby
Y. E. Imbert
M. R. Gaylord

Technical Objective:

To understand the mechanical behavior of materials at elevated temperature, with special emphasis on the influence of grain boundaries

on creep, and on the influence of a stable second phase on the strength of polycrystalline solids.

Approach:

Develop techniques for the preparation of composite materials by powder metallurgy methods. Study the mechanical behavior of solids by means of constant stress tension and compression creep tests. Evaluate elastic modulus of composite materials by dynamic resonance methods.

Research Report:

The influence of grain size on the mechanical behavior of crystalline solids at elevated temperature is not well understood. Grain boundaries may affect high temperature strength in many ways: as barriers to dislocation motion, as sources or sinks of vacancies and dislocations, and by grain boundary shearing. As the grain size is varied by means of various thermal and mechanical treatments, two additional factors that need be considered,but generally are not, are the type of boundary created and the distribution of impurities. In the case of pure copper, it has been shown that the influence of grain size on the steady state creep rate is negligible except for very fine grain sizes when grain boundary shearing becomes important. On the other hand, the steady state creep resistance of monel metal is an important function of the thermal-mechanical treatment used to obtain a given grain size.

The high temperature strength of metallic alloys can be improved by the addition of fine particles of a second hard phase. Research is underway on the mechanism of strengthening of zinc composite materials. The deformation behavior of zinc containing fine particles of alumina (0.2 microns) in large amounts (15 volume percent) is highly anomalous. The room temperature strength of zinc is decreased by the presence of the alumina particles. At temperatures above 100°C, however, the zinc-alumina composites are considerably stronger than pure zinc. In addition, the zinc-alumina composites exhibit an inverse strain rate effect in the temperature range 200-250°C and a similar effect is observed at 375 to 400°C. Stress-strain curves exhibit strong serrations at 0.9 Tm

and at strain rates of about 0.3 per minute. It is intended to study the structure of such composites by electron transmission microscopy and by ordinary metallography in order to elucidate the peculiar behavior observed.

The influence of a second phase on the strength and ductility of magnesium has been initiated. Composites of magnesium containing tungsten and magnesia are being prepared by powder metallurgy techniques.

(2) Influence of Point Defects on the Mechanical Behavior of Solids

(with O. C. Shepard, Professor, Materials Science)

Graduate Students: M. D. Merz
C. M. Packer
J. S. Perrin
S. L. Robinson

Technical Objective:

To study the possible influence of point defects on the mechanical behavior of solids and to evaluate the vacancy generation during plastic deformation at elevated temperature.

Approach:

Constant stress creep tests, constant strain rate tests, and chemical diffusion methods were used to study the possible importance of non-equilibrium point defects on mechanical behavior of materials.

Research Report:

An extensive study of the superplastic properties of Zn-Al alloys is underway. Under suitable conditions, there is an optimal range of strain rate over which a material can deform superplastically. These suitable conditions must include a fine grain size of the order of a few microns, which must remain fine grained, and a sufficiently high temperature and appropriate strain rate for continuous recrystallization to take place. In our model, deformation by slip is continuously balanced by recrystallization; essentially strain free materials is

continuously generated and the material deforms superplastically. At high strain rates the rate of recrystallization cannot keep up with the deformation process leading to elongated grains, necking of the sample and ultimate failure. At low strain rates insufficient strain energy is introduced to result in continuous recrystallization.

It has been shown that the power law for creep of pure polycrystalline metals breaks down at a strain rate of $10^9 D_u$ where D_u is the static diffusion coefficient in units of cm^2/sec. Above $\dot{\epsilon} = 10^9 D_u$ it is believed that vacancies are generated mechanically, contributing to a creep rate greater than the creep rate predicted from extrapolation of the power law range. Detailed analyses of the creep behavior of pure polycrystalline tungsten suggests that steady state creep of pure metals is proportional to an effective diffusion coefficient involving dislocation short-circuiting and lattice diffusion; in the power law range the creep rate appears to be proportional to the subgrain size squared and to the seventh power of stress.

(3) Mechanical Behavior of Polycrystalline Non-Metallics at Elevated Temperatures

Graduate Students: P. M. Burke
W. R. Cannon
Y. Miyazawa

The creep behavior of polycrystalline high purity sodium chloride has been evaluated as a function of temperature, stress and grain size. In addition, studies have been completed on solid solution alloying effects on creep of polycrystalline sodium chloride; specifically, the system NaCl-KCl was investigated.

The results obtained to date indicate that the creep rate of polycrystalline sodium chloride is controlled by the rate of diffusion of chlorine ions. The same creep formulas that have been developed for polycrystalline metals are directly applicable to describing the creep of polycrystalline sodium chloride suggesting that dislocation climb is the rate-controlling creep process. The mechanical behavior of polycrystalline NaCl-KCl solid solutions appears to be controlled by a dislocation glide process and follows the same pattern as is observed for many metallic solid solutions.

The creep of polycrystalline alumina will be studied at temperatures above 1200°C. It is intended to establish the relative importance of Nabarro-Herring deformation, grain boundary sliding grain boundary separation, slip and polygonization during the creep of alumina.

(4) Deformation of Materials at High Strain Rate at High Temperatures

(With O. C. Shepard, Professor, Materials Science)

Graduate Students: A. M. Gaylord
M. J. Harrigan
A. R. McIlree
J. Readio

Steels are generally hot worked high in the austenite range (1800-2300°F). This is the temperature range where steels exhibit high ductility and their resistance to plastic flow is low. It is now known, however, that low carbon steels can also exhibit high ductility around 1200 to 1500°F, in the stable ferrite region. In this temperature range subgrains will develop whose size depends on the strain rate and temperature. A study was initiated on the influence of subgrain formation in low carbon steels (obtained by warm rolling) on the subsequent strength and ductility characteristics at low and ambient temperatures. A 0.1 per cent carbon steel was investigated at three different initial austenitic grain sizes. Preliminary results suggest that warm working improves the strength of low carbon but the impact resistance is decreased slightly.

The factors influencing ductility and ductile fracture of materials at elevated temperature have not been studied extensively. Such studies are of paramount importance in assessing the formability of materials. A torsion apparatus has been developed at Stanford capable of deforming materials up to strain rates of 10,000 percent per second and temperatures of up to 2600°F. It is intended to study the influence of strain rate and temperature on the structure developed in several technological materials (Udimet 700, D6-AC alloy and Ti-6 Al-4V). The type of microstructure produced in the torsion tested samples will be compared with the structure obtained by hot extrusion at comparable strain rates and temperatures.

Reference Publications:

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2. C. M. Packer and O. D. Sherby, "An Interpretation of the Superplasticity Phenomenon in Two-phase Alloys," Trans. ASM 60, 21-28 (Mar. 1967).

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35. MAGNETIC DOMAIN WALLS IN THE ORTHOFERRITES

W. Shockley, Alexander M. Poniatoff Professor of Engineering and Applied Science

Graduate Student:

A. J. Kurtzig

Agency Support:

ONR Nonr 225(83)

Technical Objective:

The purpose of this project is to control the magnetic domain walls in the orthoferrites and then to measure some of the wall properties.

Research Report:

Several new techniques to control the domain walls have been achieved. For example, the simplest possible domain structure (planar, parallel, equally-spaced walls) has been achieved by two independent techniques. This wall configuration is observed to be the most stable configuration in carefully prepared and properly oriented samples. This wall configuration has also been observed to be a stable configuration in samples which are not so oriented if the spacing between the neighboring walls is small enough.

A new technique has been achieved to measure the domain wall energy per unit area. This new technique is more precise than the previously reported technique, which is based on the spacing between neighboring domain walls in the most stable domain structure for a sample. In the new technique, the planar, parallel, equally-spaced walls, which were described earlier, have been controllably stretched by an external magnetic field to increase the wall area and wall energy within the sample. Calculation of the work exerted by the applied magnetic field to stretch the walls yields the new measurement of the

domain wall energy per unit area.

Improvement of the technique to measure the wall energy per unit area is now under way. It should then be possible to use this measuring technique to develop a better understanding of the magnetic state of the orthoferrites.

36. KINETICS OF SOME SOLID STATE REACTIONS

J. C. Shyne, Professor, Materials Science

Research Associate: E. A. Attia

Graduate Students:

R. J. Austin
J. R. Costa-Guimaraes
F. C. Fehrer
F. F. M. Lee
D. O. Nason
K. Nishioka

Agency Support:

NSF GK 836
ONR Nonr 225(60)
ONR N14-67-A 0112-0021
AF F33615-67-C-1512
ARPA SD-87

Research Report:

(1) Phase Transformations in Metals and Alloys

Graduate Students: J. R. Costa-Guimaraes
D. O. Nason

Technical Objective:

A study of the kinetic, crystallographic, and morphological features of phase transformations in solid metals to elucidate the transformation mechanisms.

Approach:

Observation of the time and temperature dependence of the progress, of transformations, predominantly by electrical resistivity measurements, observation of the structural features of transformed alloys.

Kinetics of the $\gamma \rightarrow \alpha$ Transition in Fe Base Alloys

Graduate Student: D. O. Nason

A variety of Fe plus Ni, Mo, C and B alloys have been prepared as

wire specimens for high velocity isothermal transformation experiments. Apparatus has been constructed which is capable of automatically changing the specimen temperature from one temperature level to another at a rate of 2500°C/sec while simultaneously recording the specimen resistivity. The isothermal transformation kinetics observed for the $\gamma \rightarrow \alpha$ transformation in Fe base alloys has been surprising. The rate of transformation appears to be affected by solutes in a thermodynamic way; the transformation is decreased only because the free energy change accompanying the transformation is lower relative to pure iron (boron appears to be an exception to this). These results are clearly at odds with the reported results of experiments on similar alloys when continuous cooling methods were used.

Internal Structure of Martensite

Graduate Student: J. R. Costa-Guimaraes

The internal structure of martensite in high Ni content Fe base alloys has been examined. The complex internal structure and irregular interfaces suggest that the growth process during the formation of martensite plates is much more complex than is often assumed for theoretical treatments of the transformation crystallography.

Alloys have been obtained for further martensite studies. In particular, the mechanical stabilization of austenite will be studied to gain further insight into the nucleation process.

(2) The Influence of High Intensity Acoustic Radiation on the Kinetics of Solid State Processes

Graduate Student: F. C. Fehrer

Technical Objective:

To observe and explain the influence of ultrasonic mechanical vibrations on the rates of some solid state reactions.

Approach:

High amplitude standing waves are developed in specimen materials

using a 20 kc transducer. Isothermal reaction rates are measured as a function of reaction temperature and accustical intensity.

Progress:

The experimental observations outlined in the progress report of one year ago have been described in technical papers and are in the process of publication.

An attempt was made to assess the influence of high intensity ultrasound on the formation of martensite embryoes. The results were negative; no significant influence was observed.

(3) Internal Friction of Materials

Graduate Student: R. J. Austin

Technical Objective:

To utilize mechanical damping measurements to study diffusional processes, internal interfaces, and dislocation behavior.

Approach:

This is essentially absorption spectroscopy in the accoustical frequency range. The decay in amplitude of specimens vibrating in free decay is measured as a function of frequency and temperature.

Some additional measurements have been made of the damping in Al-Al_2O_3, SAP, alloys. This has served only to confirm the conclusions reported in last years report.

An inverted torsion pendulum has been constructed and completely calibrated. This is to be used for the study of thermally activated dislocation movement. Wire specimens of high purity Au and Al have been prepared with a bamboo grain structure for this purpose.

(4) The Stress Dependence of Dislocation Velocity at High Temperatures

(With W. D. Nix, Associate Professor, Materials Science)

Graduate Students: W. A. Coghlan
R. Gasca-Neri
F. F. M. Lee
K. Nishioka
A. A. Solomon

Technical Objective:

To measure the stress dependence of dislocation movement rates at high temperatures. This will contribute to the understanding of elevated temperature plastic properties.

Approach:

Single crystal specimens are tested mechanically. Stress relaxation data are related to dislocation distribution and density to obtain the dislocation velocity dependence on stress. Four materials are being studied: LiF, Al, Fe-3Si, and Zn.

Progress:

To date, efforts have been restricted to equipment development and preparation of suitable single crystal specimens.

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2. K. R. Kinsman and J. C. Shyne, "Thermal Stabilization of Austenite in Fe-Ni-C Alloys," Acta Met. 15, 1527 (Sept. 1967).

3. R. D. Nelson and J. C. Shyne, "The Mechanism of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ Transformations in Plutonium," Trans. AIME 236, 1725 (Dec. 1966).

4. T. D. Gulden and J. C. Shyne, "Internal Friction of Alkali Metals I. Nominally Pure Potassium and Sodium," Metal Science Journal (in publication).

5. T. D. Gulden and J. C. Shyne, "Internal Friction of Alkali Metals II. Zener Relaxation in Potassium-Rubidium Alloys," Metal Science Journal (in publication).

6. G. A. Hayes and J. C. Shyne, "The Influence of Ultra Sound on the Kinetics of Recrystallization in Copper," Trans. AIME (in publication).

7. G. A. Hayes and J. C. Shyne, "The Influence of Ultra Sound on the Kinetics of Precipitation Hardening in a Cu-Be Alloy," Metal Science Journal (in publication).

8. G. A. Hayes and J. C. Shyne, "Ultrasonic Enhancement of Grain Growth in Copper," Phil. Mag. (in publication).

37. OPTICAL AND LASER PHENOMENA IN SOLIDS

A. E. Siegman, Professor, Electrical Engineering

Graduate Students:

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D. J. Kuizenga
J. A. Tellefsen

Agency Support:

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Research Report:

(1) Nd:YAG Laser Studies

Graduate Students: D. S. Carlson
D. J. Kuizenga

A method of frequency tuning a laser over its atomic bandwidth has been developed. The frequency tuning is achieved through the use of a birefringent electro-optic crystal and a polarizer. Experiments were performed on a cw Nd:YAG laser, and frequency tuning over 130 GHz (≈ 4 Å) was achieved. Electronic polarization switching of the oscillation between two orthogonal linear polarizations is also obtained. This technique has also been used to produce laser pulses at a 3 KHz pulse repetition frequency, by Q-switching the cavity at this rate.[1]

(2) Free-Carrier Optical Absorption Effects in Semiconductors

Graduate Student: J. A. Tellefsen

Generation of free carriers in semiconductors (such as silicon) by incident high-voltage electron beams (10-30 kv) has been used to accomplish modulation and image detection of infrared (IR) laser signals and to study free-carrier IR absorption in semiconductors.

A new configuration for this type of device has been conceived which should minimize optical losses and maximize interaction between the IR beam and the free electrons. An initial model of our experimental

device is complete and it is hoped that successful operation is imminent.

Reference Publication:

1. D. S. Carlson and A. E. Siegman, "Intracavity Electro-optic Frequency Tuning, Polarization Switching, and Q-switching of a Nd:YAG Laser Oscillator," J. Quant. Elect. (submitted for publication).

38. X-RAY DIFFRACTION STUDIES OF MOLECULAR AND CRYSTAL STRUCTURE

P. G. Simpson, Assistant Professor, Chemistry

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Agency Support:

ARPA SD-87

Technical Objectives:

The objectives of this program are to develop improved methods of structure determination from diffraction data and to determine the detailed three-dimensional structure of several crystalline materials, including biological molecules.

Approach:

The three-dimensional X-ray diffraction data collected from single crystals converted into a inter-atomic vector map by Fourier synthesis. High order superposition functions derived from this vector map are studied and used to solve the detailed crystal structure. In order to prepare suitable crystals of a protein heavy atom derivative for X-ray analysis, protein interaction with metal salts is studied titrimetrically.

Research Report:

(1) Vallesamidine, an alkaloid isolated by A. Walser in C. Djerassi's laboratory, has been shown by them to be an isomer of N(a)-methylaspidospermine. Our crystal structure analysis[1] shows that the molecule

has a sterochemistry unique in the class of aspidospermine alkaloids.

Crystals of the methyl iodide salt were obtained from which complete three dimensional X-ray diffraction was collected by film methods. The relative intensities were estimated visually and the data were reduced, scaled, corrected for Lorentz and polarization effects, and analyzed for individual standard deviations. Errors in the data due to X-ray absorption were large and attempts to make general corrections were not satisfactory. It was initially felt that the data were sufficient to establish the structure within the accuracy needed.

The positions of the two iodine atoms, related by the two-fold screw axis of the groups $P2_1$, was found easily from the largest peak in the interatomic vector map. Three functions were examined for possible positions for the twenty-seven unique carbon, nitrogen and oxygen atoms in the crystal structure: the interatomic vector map, the approximate electron density map based on the iodine phases for the structure factors, and the second order addition function based on the iodine positions. The approximate electron density function was the easiest of the three functions to interpret. The three functions yielded consistently a model for the complete crystal structure except the solvent molecule and the hydrogen atoms. This model was refined by least squares fitting of the observed and calculated diffraction intensities. The solvent molecule was located during the refinement, completing the non-hydrogen crystal structure. The final agreement factor, $R = \Sigma \mid F_{obs} \mid - \mid F_{calc} \mid / \Sigma \mid F_{obs} \mid$, was 0.184 using all the data. This is believed to be the limit of the data which is badly affected by absorption.

There are two problems with this structure model. First, the uncertainities in the bond distances and angles are rather large. The second problem is more serious: There is a mirror plane which is present in the iodine atom partial structure but not in the complete structure. This psuedo-mirror plane runs through about the middle of the alkaloid molecule and produces a two-fold ambiguity in the location of atoms from junctions based on the iodine partial structure. Several

attempts were made to resolve this ambiguity by various methods. This most sophisticated approach was a new extension of superposition techniques using all the light atom positions. This purely objective approach was not definitive and did not yield a chemically meaningful structure. An analysis of the possible structures making use of known interatomic bond distances and angles leads us to favor a particular molecular structure for the alkaloid; however, there is another model which has the same atomic skeleton but different sterochemistry at the ring junctures which can not be entirely eliminated. In either case the skeleton is the same and differs from known aspidospermine alkaloids.

These difficulties undoubtedly arise from the poor quality of the film data caused by high absorption effects. Hence, we decided to collect a new set of data without absorption problems by using a much smaller crystal and harder X-rays - MoKα instead of CuKα. This data has been measured on the automatic X-ray diffractometer recently acquired through ARPA SD-87 support. This data is now being prepared for crystal structure analysis.

(2) Crystals of the 1:1 π-complex between chlorpromazine and 7,7,8,8 - tetracynoquinodimethane have been prepared and are suitable for crystal structure analysis. These crystals are twinned, but yield a much cleaner diffraction pattern than the similar crystalline π- complexes that we have obtained. The unit cell contains two molecular pairs. Since the diffraction pattern is complicated somewhat by the twinning, a complete film record of the data is being made now before collecting more accurate diffractometer data.

(3) Our study of ubiquinone 50, an electron carrier in the oxidative phosphorylation chain, is being continued. Samples of this lipid quinone containing sixty-three carbon and oxygen atoms have been purified by thin layer chromatography and crystallized from ethyl acetate. The crystals appear under microscopic examination to be well formed thin flat plates. Larger, especially thicker, crystals are needed in order to measure the diffraction data.

(4) Our crystallographic study of tuna fish cytochrome c is continuing. Crystals of the native protein have been grown which show diffraction maxima down to a Bragg spacing of about 2-5 Å on oscillation photographs with CrKα radiation. We will now attempt to orient crystals on the automatic diffractometer and measure reflection intensities.

Reference:

1. S. H. Brown and P. G. Simpson, Abstracts of the Winter Meeting, 1967, of the American Crystallographic Assn., Paper F7.

39. PHOTOEMISSION AND ELECTRONIC STRUCTURE OF SOLIDS

W. E. Spicer, Professor, Electrical Engineering and Materials Science

Graduate Students:

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ARPA SD-87

Technical Objective:

To study the electronic structure of solids using photoemission and optical absorption techniques. It is hoped that contributions can be made to understand such diverse phenomena as ferromagnetism and the cohesive energy of solids through a better understanding of the electronic states in solids. Another objective is the optimum coupling of the basic results to practical utilization by government agencies.

Approach:

Measurement of the spectral distribution of the photoemission quantum yield and the energy distribution of the emitted photoelectrons using visible, near- and vacuum-ultraviolet spectra. Measurements are also made of the optical properties of the solids when this is not available from the literature. The coupling effort is obtained both through government contracts when the capabilities developed through the basic work can be applied to a specific need, and through presentations at and other communications with industrial and government laboratories concerned with the subjects covered.

(1) Electronic Structure of Noble and Transition Metals and Its Relationship to Ferromagnetism

The principal object of this study is to determine the optical density of states of the noble and transition metals and to relate these results to the understanding of ferromagnetism in metals through the determination of the optical density of states.

"Photoemission and Optical Studies of
Pd, Pt, Co and Gd"

Graduate Student: A. Y-C. Yu

Photoemission and optical reflectivity measurements on cobalt, palladium, platinum, and gadolinium have been made to determine the major features of their electronic structures. Nondirect transitions predominate the optical transitions in all of these materials; however, direct transitions (or nondirect transitions with varying matrix element) are also observed in palladium and platinum.

The optical density of states of cobalt is found to be very similar to that of nickel and iron, despite the fact that all three metals have different crystal structures. They all have a strong peak at about 5 eV below the Fermi level. No such peak is present in the optical densities of states of palladium and platinum at this energy, though the latter has a strong peak at about 7 eV below the Fermi level. This deep valence band peak has not been predicted by older band calculations. Consequently, it has been suggested that the origin of this probably lies outside of the one-electron band theory. Recently, band calculations of nickel using different exchange potentials predicted such a low energy peak in the density of states.

The optical density of states of palladium and platinum all have strong peaks right below the Fermi level, in reasonable agreement with the findings based on specific heat and magnetic susceptibility data. The noble metals, copper, silver and gold, also have strong peaks near the top of the d states.

The optical density of states of gadolinium is found to be in reasonable agreement with the calculated density of states for $-4 \text{ eV} \leq E - E_f \leq 0$. A strong peak located at $E - E_f = -6.5$ eV is probably due to f electrons. A peak at $E-E_f = 3$ eV is also located in the conduction band.

"Photoemission and Optical Studies of Copper-Nickel Alloys"

Graduate Student: D. H. Seib

Alloys of copper and nickel of varying composition are being studied using photoemssion and optical techniques. Investigation of this alloy system is part of a systematic study of the 3d transitional elements and noble metals. Alloys of copper and nickel in the range 50 percent to

100 percent nickel have a spontaneous magnetic moment which has magnitude linear with composition. Thus studies of alloys in this region might contribute to an understanding of ferromagnetism. In previous photoemission work on nickel a large, unexplained valence band density of states peak was found at about 4.5 eV below the Fermi level. A much smaller and much deeper anomalous peak was also found in copper. Following the behavior of this peak in copper-nickel alloys might help to clarify its origin. In addition to probing these areas, studies of copper-nickel alloys may contribute to a better understanding of the electronic states of alloys in general.

Alloy samples used in these studies are first annealed at 1000° C. for a long period of time, then cut and mechanically and chemically polished. The final cleaning of the surface prior to measurement is accomplished by heating the samples in vacuum for several hours at temperatures of about 500°C. Using this sample preparation technique pure copper and pure nickel were studied, with results identical to those previously obtained using evaporated films of these materials.

To date alloys of compositions 70%Cu-30%Ni and 70%Ni-30%Cu have been studied. The reflectivity of 70Ni-30Cu is quite similar to that of pure nickel, but the photoemission results are significantly different. Two peaks in the alloy valence band density of states lie at very nearly the same energy as in pure nickel, but in the alloy there is an additional peak about 1.6 eV below the Fermi level. Also in the alloy the anomalous peak lies about one eV further below the Fermi level than in pure nickel.

Photoemission results from 70Cu-30Ni indicate that the major portion of the d-states are slightly further below the Fermi level than in pure copper. Also the magnitude of the first d-band density of states peak

relative to the s and p band contribution is much smaller in the alloy than in pure copper. Results from these two alloys seem to indicate that a rigid band model does not describe properly the behavior of electronic states upon alloying, at least for the compositions mentioned.

Further work is being done on this alloy system and will include the study of several more alloy compositions, in addition to a more thorough analysis of data already obtained.

"Rhodium and Ni-Rh Alloys"

Graduate Student: D. T. Pierce

The experimental study of Rh is underway. Rhodium of 99.95 percent purity was successfully evaporated using the Varian e-gun onto a pyrex substrate while the pressure was maintained below 10^{-3} mm Hg. The present measurements which extend from 1.5 to 11.5 eV will be repeated and extended to .025 eV in the infrared and to higher energies in the ultraviolet at low vacuum. An ellipsometer may be used to obtain non-normal incidence reflectivity data which would improve the Kramers-Kronig analysis. The photoemission study of evaporated rhodium will be started soon.

Polycrystalline button samples of Ni-Rh alloys, 70Ni-30Rh and 40Ni-60Rh, are being prepared by Materials Research Corporation. The possibility of acquiring facilities to prepare such samples at Stanford is being investigated. It is expected that these two samples will give important information on the Ni-Rh system on each side of the ferromagnetic transition which occurs at approximately 63%Ni. Electro and chemical polishing techniques are being studied in connection with preparing the alloys for reflectivity and photoemission measurements.

Also being considered for investigation is the Ag-Pd alloy system. This system, from the point of view of the rigid band model, more closely parallels the Cu-Ni system, also under study in this laboratory.

(2) Photoemission and Optical Studies of Divalent Alkaline and Rare Earth Metals

Graduate Student: J. G. Endriz

Photoemission and optical studies are being undertaken on the alkaline earth metals, Ba and Sr, and the divalent rare earth metals, Eu and Yb. It is hoped that such studies will shed light on the validity of recent band calculations on the divalent rare earths and alkaline earths by Freeman, Dimmock, Animalu, et. al., indicating an anomalous drop in the density of states near the Fermi energy.

It is also hoped that comparing results obtained from the f.c.c. Sr and Yb metals and the b.c.c. Ba and Eu metals will lead to the firm establishment of the f-electron energy levels in Eu and Yb. It should be noted that Ba and Eu lie in the same column of the periodic chart, and differ only by the presence of a half-filled f-shell in Eu. Sr and Yb differ only in the presence of an extra completed shell and full f-shell in Yb. Attempts will also be made to determine the width of the 4-f levels in Yb and Eu and to reconcile these results with the relatively wide energy spread found for the f-electrons in Gd by Yu, and the rather narrow energy spread which would be expected in view of the tightly bound nature of the 4-f electrons.

Characterization of all optical transitions as either direct or nondirect will be attempted with particular interest in the selection rules governing the highly local f-electrons.

Early reflectivity results for Yb indicate that the high vacuum facilities of this laboratory are capable of yielding better structure in the infrared and visible spectral regions than was obtained in previous reflectivity

studies of these divalent materials. Preparation of all the above materials is accomplished by evaporation, and present studies are involved in the determination of appropriate substrate materials and evaporation techniques.

(3) Studies of Indium in the Crystalline, Noncrystalline and Liquid States

Graduate Student: R. Y. Koyama

In the theoretical development of the electronic band structure of solids, crystal symmetry and translational periodicity have played important parts. As such, it is of interest to determine experimentally the extent to which the crystal lattice influences the electronic properties.

The technique of photoemission is being used to probe the electronic bands of the metal indium using samples of different lattice forms; namely, the following forms have been studied: the polycrystalline solid, the thin film solid, the solid formed from the melt, and the liquid. If the electrons are strongly affected by the presence of the lattice, one might expect to see some differences in the electronic states when comparing the polycrystalline solid and the liquid.

In a free electron metal, the density of states monotonically increases and is proportional to $E^{1/2}$. When the lattice potential is turned on, band gaps appear at the Brillouin zone boundaries. Depending upon the position of the Fermi level, these band gaps could change the density of occupied states. Indium is a trivalent metal and thus has its "free electron" Fermi surface about 8.5 electron volts above the bottom of the lowest. Since the free electron sphere reaches into parts of the fourth zone, the density of states would be altered by the gaps due to boundaries of the four zones. Experiments on polycrystalline samples of indium indicate that the optical density of states shows a definite departure from the free electron case in that strong structure appears in the photoemission energy distributions.

Interaction of the electrons with the lattice can take place through one or both of two ways: interaction with the crystal as a whole (long-range interaction), or interaction with individual or a small collection of ion sites (short-range interaction). The crystalline solid provides the basis for discussion of Brillouin zones which depend on long-range ordering. On the other hand, the liquid has no such long-range ordering although it must have some short-range ordering. Photoemission measurements on the liquid samples show structure which is similar to that seen in the crystalline solid. The similarity of the results for the two samples would suggest that (1) the lattice potential was essentially the same in both cases, and that (2) owing to the disordered nature of the liquid, short-range interaction is more dominant than long-range interaction in determining the photoemission properties.

(4) Ellipsometry and Photoemission Measurements on Alkali Metals

Research Associate: N. V. Smith

Recent measurements by Mayer and Hietel suggest that the optical behavior of the alkali metals is not as simple as had hitherto been believed. Our aim is to repeat these measurements and also use the powerful photoemission technique to provide further information on the nature of optical transitions in these materials. So far, an ellipsometer has been built and operated successfully in the photon energy range 0.5 to 4.0 eV, and some trial results on indium have been obtained. A vacuum chamber and flange in which the metal samples will be prepared has been built. It will be evacuated by a Varian Noble Vacion pump on which tests are presently in progress.

A project (in collaboration with Mr. G. Fisher) to build a polarizer for the far ultraviolet is also underway. We intend to use this in a study of photoemission on a single crystal of CdS which is non-cubic. Conventional theory of the direct transition would lead one to expect a variation in the magnitude of the optical matrix elements as the orientation of the incident electric vector is rotated.

While waiting for equipment, computer calculations have been performed, and are still in progress, to obtain numerical values for the following quantities:

1) Eigenstates and optical absorption of liquid Na -- an article covering this is in press with the Physical Review,
2) Density of states, optical absorption, electron-ion scattering and Knight Shift in liquid and solid metals and alloys,
3) Effects of electron-electron scattering on photoemission energy-distributions in simple metals.

5. Photoemission Studies of the Noble Metals, the Alkali Halides, and the Cuprous Halides

Graduate Student: W. F. Krolikowski

The possible presence of the copper d band in the valence band of the cuprous halides has been largely ignored in the recent literature, and structure in the optical spectrum of the cuprous halides has been associated with direct transitions between symmetry points in a germanium-like band structure. In order to test the validity of these explanations for the optical spectrum of the cuprous halides, the electronic properties of the cuprous halides have been investigated in detail by use of experimental photoemission techniques. The quantum yield and photoemission data

resulting from these photoemission measurements have been interpreted in terms of the electronic structure of the cuprous halides, and it is found that the copper d band plays a significant role in the valence band of the cuprous halides.

In order to distinguish the copper d band from the halogen p bands in the cuprous halides, it was found useful to extend the photoemission studies to the noble metals and the alkali halides. Consequently, this report includes not only studies of the cuprous halides (CuCl, CuBr, CuI), but also detailed studies of the noble metals (Cu, Ag, Au) and certain alkali halides (CsCl, CsBr, CsI, and KI). Some of the most important results of this work are summarized below:

(1) The experimental quantum yield and photoelectric energy distributions have been measured for all the materials in the range of photon energies below 11.6 eV. In several cases, the measurements have been extended to photon energies as high as 21.2 eV.

(2) For nearly all of the materials, the optical density of states has been determined in the range of energies between 11.6 eV below the Fermi level and 11.6 eV above the Fermi level.

(3) Nondirect transitions are found to dominate the optical absorption process in the noble metals and the cuprous halides. Direct transitions are found to have secondary importance compared with nondirect transitions.

6. Optical Properties of Alkali Halides

Graduate Student: T. D. DiStefano

Photoemission from alkali halides is complicated by the high resistivity of the sample. In a sufficiently thin film, however, the surface of the film is found to remain uncharged while electrons are photoemitted from it at a small current density. This, of course, requires special equipment. A device to determine the thickness of these extremely thin films was built and successfully used. The measurement of the

comparatively small currents involved required the construction of noise minimizing electronics: a noise free retarding voltage sweep, a generator to drive the lock-in amplifier at a subharmonic of sixty cycles, and the appropriate noise filters.

From this work, some knowledge of the localized valence electrons in alkali halides is anticipated. These valence electrons are thought to be below the Mott transition; this can be checked by looking at hole mobility in thick films, and by a comparison of the optical properties of the alkali halide alloys in comparison to those of the pure components of the alloy. Work is under way on an evaporator for the simultaneous deposition of two different alkali halides; this will be an essential piece of equipment for the photo-investigation of the alloys.

7. Photoemission and Optical Studies of the Electronic Structure of NiO, CoO, and V_2O_4

Graduate Student: R. J. Powell

The nature of the electronic states in the transition metal oxides has been the subject of controversy for some time. The difficulty arises because some of these oxides are insulators, and conventional band theory predicts that they should be metallic conductors because of their partially filled states. Models based on band theory, which have been proposed to explain this behavior, depend upon magnetic ordering. Localized models, on the other hand, explain the insulating nature as the result of weak interaction (small orbital overlap) of the metal ion d electrons.

Photoelectric emission and optical reflectance measurements have been performed on NiO, CoO, and V_2O_4 in order to determine details of their electronic structures and to examine the predictions of the theoretical models. Photoemission from these materials has been measured both above and below their magnetic transition temperatures.

Details of experimental techniques are presented, including a new high-vacuum cleaving apparatus used for cleaving the NiO and CoO single crystals, and a method of preparing V_2O_4.

From the results of these studies it is concluded that the highest lying filled states in the electronic structure of NiO and CoO are best represented by localized wavefunctions and that the various band models with magnetic ordering are not applicable to NiO or CoO. Evidence is presented that the highest lying filled levels in NiO and CoO are due primarily to the $3d^8$ and $3d^7$ levels of the nickel and cobalt ions, respectively, and that beneath these levels lies a band (several eV in optical width) associated with the oxygen ion 2p levels.

Over most of the energy range covered, the photoemission data on NiO and CoO are found to give excellent agreement with a model in which optical transition probability depends only upon the product of the densities of initial and final states. The optical density of electronic states in NiO has maxima at +7.5, -1.6, -5.8, and -9.2 eV (energies referred to the top of the occupied levels), and the maxima in CoO are at +8.4, +7.0 (shoulder), -1.8, -6.6, and -9.6 eV. These results are found to be in qualitative agreement with an energy level calculation.

Strong similarities are noted between the NiO and CoO optical densities of states, but in CoO significant optical selection rules are observed in photoemission for initial energies less than -2.5 eV. Such variations are not apparent in NiO.

The optical constants of NiO and CoO have been determined for photon energies from 1 to 26 eV by a Kramers-Kronig analysis of their reflectance spectra. Positions of structure in their optical constants are consistent with the maxima in their respective optical densities of states

determined from photoemission data. Measurements have indicated the absence of photoconductivity in NiO with the presence of strong optical absorption in the photon energy range from 4 to 7 eV. This is interpreted in terms of localized charge-transfer excitations.

The photoelectric yield of V_2O_4 displays an abrupt change at the 67°C transition temperature. Photoelectron energy distributions show that the relative positions of the Fermi and vacuum levels are the same at 25°C and 100°C, while the top of the filled levels is 0.6 eV lower in energy (relative to the Fermi and vacuum levels) at 25°C than at 100°C. For photon energies in the range $2 \leq \hbar\omega \leq 5$ eV, the 100°C reflectance falls below the 25°C values.

8. Photoemission Studies of the Electronic Band Structures of Gallium Arsenide, Gallium Phosphide and Silicon

Research Associate: R. C. Eden

Photoemission measurements on single crystals of gallium arsenide, gallium phosphide and silicon have been completed and the data analyzed. These materials are especially interesting for study, since their electronic band structures have been extensively studied on both experimental and theoretical bases. This background of knowledge makes it possible to interpret in detail the results of photoemission measurements in terms of features of calculated band structures for these materials, and conversely to measure the accuracy of the calculated band structures by means of the photoemission results. These measurements of photoemissive yield and energy distributions for photoemitted electrons, as a function of the photon energy of the monochromatic light were made both on clean surfaces of GaAs, GaP and silicon, and on surfaces covered with a monolayer of cesium to lower the vacuum level. By using monochromatic light with photon energies

up to 11.9 eV, it was possible to study the range of electron final energies from 11.9 eV above the top of the valence band down to the bottom of the conduction band for GaAs and GaP or to near the bottom of the conduction band for silicon (with cesiated surfaces). The initial valence band states observable for this range of photon and final electron energies extend from about 9 eV below the valence maximum up to the valence band maximum.

The structure features of the energy distribution curves for photoemitted electrons for GaAs, GaP, and Si have been explained in detail in terms of direct interband transitions in the respective electronic energy band structures of the materials. The final energies of energy distribution structure predicted from calculated electronic band structures for these materials were found to be in good over-all agreement with the experimentally observed structure energies. In the analysis of this photoemission data, it was observed that the effect of surface band bending on the energy distributions of emitted electrons was quite significant. Techniques for correcting for bending effects in photoemission data were developed and employed in the analysis of this data.

The over-all photoemission results for the three materials were found to be quite similar, which reflects the basic similarity of their electronic band structures and optical spectra. Many different energy band features were observed in the data for each material. For example, in GaAs the energy band features identified include (using the symmetry point or line symbol followed by the number of the energy band to identify the features, where the bands are numbered upward starting with the deep valence band) Γ_1 (5), Γ_{15}(6, 7, 8), Γ_1 (9), Γ_{12} (10, 11), L_2 (2), L_3 (3, 4), L_3 (6, 7), X_5 (3, 4), X_1 (5), band 3 minimum (near K), band 8 inflection

point (along Γ), and the band 9 minimum along Γ. In addition, the levels involved in the major optical transitions were observed and additional direct transitions and conduction band structure features not along the major symmetry lines are observed. Most of these levels are also observed in GaP and Si and some additional levels as well, such as $X_3(2)$ in GaP. A final report on this work has been prepared.[1,2]

An important aspect of this work over and above the band structure implications mentioned above involves photoemission from cesiated p^{++} GaAs in the visible and near infrared portions of the spectrum. This photocathode is of great practical interest because of the extremely high quantum yields it exhibits. However, the difficulties in preparing and maintaining high-yield photocathodes of this material observed in this and other laboratories point up the need for further study on this photosurface. A great deal of information about the fundamental electronic processes involved in photoemission from this material has been gained.[3,4,5] In particular, the high quantum efficiency has been basically reproduced and the limiting factor found to be the diffusion length of electrons in the material. It was found that pressures of less than 10^{-10} torr were necessary to obtain this result. Further studies are continuing in this laboratory.

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3. R. C. Eden, J. L. Moll, and W. E. Spicer, Phys. Rev. Letters, 18, 15 597, 1967.

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"Studies of GaSb and Surface Effects of Cs"

Graduate Student: A. D. Baer

The design and construction of a new chamber and pumping system for the purpose of obtaining and maintaining atomically clean surfaces on crystals has been completed. With this chamber, it has been possible to achieve a much more nearly planar cleave along a (110) face of a $1cm^2$ GaAs crystal than was achieved with previously existing systems. In fact there were no steps over most of the cleaved surface. Cleaves have been achieved while the system was maintained at pressures of less than 10^{-10} torr. Pressures maintained during measurements were typically $2\text{-}4 \times 10^{-11}$ torr. At this pressure the time constant necessary for formation of a monolayer on the cleaved surface is on the order of one week, assuming a sticking coefficient of .01 (sticking coefficient of O_2 on Si),[1] whereas measurements can be made within a few minutes of cleaving. There is reason to believe that sticking coefficients of residual gasses normally found in vacuum systems are less than 10^{-5} for the (110) faces of GaAs and GaSb.[2] Consequently the surfaces studied using this system should certainly remain atomically clean during the entire measurement period of one week. Experimentally, we have found no evidence for surface contamination during measurement.

Photoemission measurements will be performed on a crystal of GaSb in the near future. These measurements will be used in a study of the surface effects of Cs and in a study of the electronic band structure

of GaSb. Currently there is substantial disagreement in the literature concerning the band structure of GaSb. The positions of bands in Cohen and Bergstresser's pseudopotential model differ as much as 1.5 eV from the positions in Herman's adjusted OPW model.[3,4] The resolution of photoemission measurements is good enough that it should be possible to determine clearly which of these band models is consistent with exper ment. Preliminary study of a gun for uniformly depositing controlled amounts of Cs is in progress.

References:

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9. Photoemission Studies of Ordered and Disordered Semiconductors

Graduate Student: T. M. Donovan

A photoemission study has been made on single crystal Ge preliminary to a study of disordered Ge films. These measurements have been made on clean surfaces cleaved in high vacuum and on cleaved surfaces with a monolayer of cesium on the surface. The range of photon energies studied was 2 - 12 eV allowing details of the electronic structure to be observed from about 10 eV above the valence band maximum to about 8 eV below this level.

Sharp structure was observed with the clean surfaces at energies greater than 7 eV where no features are observed in the optical response. It is found that these features can be interpreted as direct transitions and agree well with features in calculated energy bands. Also because the photoemission experiment can locate initial and final state energies, structure observed in the optical data and ambiguously assigned was located in the Brillouin zone unambiguously in this experiment.

With a monolayer of cesium on the surface, the work function is lowered from 4.8 to 1.8 eV. It was found that features observed at high energies with the clean surfaces are the same, indicating that all the cesium did was lower the work function. The additional features or structure revealed at lower energies can also be interpreted in terms of direct transitions and agree well with the calculated energy bands and with the optical data.

A technique has been developed for producing disordered Ge films by vacuum evaporation. Also, a method has been worked out for measuring the relative reflectance (in the range 2-6 eV) of liquid metals and semiconductors with high melting points that can be heated by r.f. induction. This system has been tested using liquid Cu.

"Studies of CdTe, CdSe, CdS, and ZnTe"

Research Assistant: J. L. Shay

Photoemission studies of CdTe, CdSe, and CdS have been completed. The results of these studies have been analyzed in terms of direct and nondirect transitions. Papers covering these results have been prepared for publication. Work on ZnTe is nearing completion and will be written up. In general a number of direct transitions have been observed and identified in these studies; in addition, optical density of states have been obtained from analysis of the nondirect transitions.

"Photoemissive and Optical Studies of
Organic Materials -- the Phthalocyanines"

Graduate Student: B. H. Schechtman

Photoemission and optical studies have been performed on a number of organic molecular solids in the phthalocyanine and porphyrin classes. These solids, in which the binding between individual molecules is of the weak van der Waals variety, are expected to be examples of materials in which nondirect processes are dominant in the optical transitions. Nondirect transitions occur when the electron and/or hole wavefunction cannot be well described by a single one-electron Bloch function. In molecular crystals with small intermolecular overlap, we would expect that (for the hole at least) the wavefunction must represent a somewhat localized state and not a Bloch state.

Besides providing materials with which we can test the above statements, the phthalocyanines and porphyrins are of particular interest because of their similarity to the biological molecules hemoglobin and chlorophyll. They are also unusually stable for organic materials and are capable of being evaporated in vacuum without dissociation. These sample properties are necessary for the performance of the photoemission experiments.

The photoemission chamber built last year has been used for most of the recent work. New data for copper phthalocyanine has been analyzed to determine the optical density of filled states. Three peaks appear, at 0.5, 3.0, and 5.4 eV below the highest filled states. As expected, all the structure is consistent with the nondirect transition model discussed above. We have measured the optical properties of copper phthalocyanine and its behavior at high photon energies has been correlated to the photoemission results.

Studies were also undertaken on metal-free phthalocyanine and nickel phthalocyanine. The results indicate that the presence of the central metal atom on the molecule is not important in determining the optical transitions seen in photoemission. We have also successfully purified and done photoemission and optical absorption experiments on chlorinated copper phthalocyanine and on protoporphyrin. The emphasis in this work was to discover which portions of the complicated phthalocyanine molecule contribute the electrons that take part in the optical and photoemission events.

The key results to date are as follows:

(1) For all the materials studied all the structure seen in photoemission can be associated with nondirect transitions.

(2) The main features of the optical density of filled states are similar for all the materials.

(3) The electrons seen in photoemission appear to come from the internal carbon-nitrogen chelate ring structure of the molecules. This is significant because it is precisely in this ring structure that the molecules studied are so similar to hemoglobin and chlorophyll.[1,2]

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10. Theoretical Study of Solids

Research Associate: K. K. Thornber

The first part of the year was occupied primarily with extending the work on polaron motion in an electric field reported in my thesis[1] to prepare it for publication. The major achievement of the work was the prediction of the maximum energy loss for an electron strongly interacting with the longitudinal optical modes of a polarizable crystal. For Al_2O_3 a loss of .025 eV/Å was obtained in good agreement with the .02 to .03 eV/Å found experimentally. Predicted values for MgO and BaO also agree with recent experimental results. In a single curve (for each lattice temperature) we display the energy loss per unit distance as a function of electron velocity from very weak fields, where the usual linear mobility theory applies, through the threshold region for optical phonon scattering which previously was unknown, to the fast or hot electron region, which also is approachable with perturbation theory.[2]

Sporadically our work on the tunneling time of an electron was sufficiently clarified and expanded for publication.[3] This controversial and widely misunderstood aspect of electron tunneling, the tunneling time, was the source of erroneous physical notions and unrealistic potential device application. The work pointed out the origin of this confusion, established the equivalence (equality) of the transition time, interaction time, tunneling time, and device RC-time constant; it disposed of the transmission time, the commonly thought of tunneling time, as being without physical meaning.[3]

The bulk of my effort, however, has been devoted to a study of the foundations of the theory of optical properties and photoemission.[4-8] The major barrier to our understanding is this. For many years a calculation

of the wavefunctions for the electrons in a material has followed from minimizing the total energy. This is probably all right if energy levels are desired. But using this procedure one has no assurance that other physical properties calculated from wavefunctions so obtained are as good as one can do. The photoemission experiments of Professor Spicer's group indicate something much better is necessary. I have attacked this problem looking both for a "variational" principle for properties other than energy and for more basic approaches to solid state physics than one-electron Bloch theory.[8]

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5. "Optical Properties of Liquid Mercury, Theory," in preparation.

6. "Photoemission Studies in Alkali-Halides, Theory," in preparation.

7. "Photoemission Studies in Transition Metal Oxides, Theory," in preparation.

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40. THERMODYNAMIC PROPERTIES AND DEFECT STRUCTURE OF SOLIDS

D. A. Stevenson, Associate Professor, Materials Science

Graduate Students:

P. M. Borsenberger
W. D. Callister
M. Müller-Henneberg
T. L. Larsen

Agency Support:

AEC AT(04-3)-283
ARPA SD-87

Research Report:

(1) Thermodynamic Properties and Defect Structure of Intermetallic Compounds

Graduate Students: P. M. Borsenberger
T. L. Larsen

Technical Objective:

The objective of this investigation is to elucidate the methods of controlling and characterizing point defects in binary compounds and to show theinfluence of such defects on properties.

Approach:

In this study, the point defect concentration is controlled by annealing pure single crystals of the compound in question in atmospheres which fix the chemical potential of the components at well defined values. The variation of defect concentration is determined by measuring the change in the self-diffusion coefficients of the component atoms and the change in the carrier density for crystals annealed under different conditions. The experimentally observed variation is compared with predictions based on postulated defect equilibria in order to establish the dominant defects in the solid. The current research effort involves self-diffusion studies in cadmium telluride and cadmium selenide and the electrical and optical properties of zinc telluride

Research Report:

The self-diffusion research has involved the measurement of the self-diffusion coefficients of Cd^{109} in CdSe and Cd^{109} and Te^{123} in CdTe. The self-diffusion measurements were performed as functions of temperature, component pressure, and added impurity content. The samples used were single crystal sections which were pre-diffusion annealed under precisely the same conditions of temperature and pressure as the subsequent tracer diffusion anneal. The experimental results suggest that: the self diffusion of Cd in CdSe involves the motion of a singly ionized Cd interstitial donor; Cd in CdTe involves ionized Cd vacancy acceptors and interstitial Cd donors; and Te in CdTe involves a neutral interstitial Te defect.

The research on zinc telluride has involved the crystal growth and control of impurity content of ZnTe and the measurement of electrical properties (resistivity and Hall effect) and optical properties (absorption coefficient, photoluminescence, and photoconductivity). One of the major items of progress during the period covered by this report is the development of a crystal growth technique for ZnTe from Te-rich liquid solutions. This solution melt growth may be accomplished at temperatures much lower than melt growth of the pure compound (~1050°C vs ~1300°C) and hence has advantages in minimizing contamination by foreign impurities. It also has the advantage of facilitating impurity additions, in contrast to vapor growth techniques. It has been possible in the past year to prepare crystals that are n-type high resistivity by using this growth technique with Al additions.

(2) <u>The Influence of Alloying Elements on the Carbon Activity in Austenite</u>

Graduate Students: W. D. Callister
M. Müller-Henneberg

Technical Objective:

To determine the influence of substitutional solutes on the carbon activity in iron base solid solutions.

Approach:

A selective carbon transfer medium was developed in which carbon in a binary iron-carbon steel is selectively equilibrated with carbon in a ternary steel alloy. Referring to the well established data for the binary steel, the activity in theternary may be determined.

Research Report:

The influence of the substitutional solute Mo on the activity of interstitial C in ternary austenitic Fe-base alloys at 1000°C was investigated. The above closed cell method was used whereby C was selectively transferred from an Fe-C alloy to Fe-Mo alloys via a carrier gas; at equilibrium the C activity is the same in all alloys. The partitioning of C between FeC and FeC-Mo alloys may be described by the simple expression

$$X_C^B = K_{X_{Mo}} \cdot X_C^T \quad ,$$

in which X_C^B and X_C^T are atom ratios of the binary and ternary alloys respectively, and $K_{X_{Mo}}$ is the slope of an X_C^B versus X_C^T plot. $K_{X_{Mo}}$ was found to be a function of Mo concentration and in all cases to be negative, which shows that Mo decreases the C activity in single phase austenite. Breakpoints in the X_C^B versus X_C^T plots were interpreted as points on the γ - γ + carbide boundary. Mo was found to have relatively small influence on the position of this boundary.

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41. FUNDAMENTAL ASPECTS OF REACTIVITY IN INORGANIC SYSTEMS

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Professional Associates:

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F. Maspero
G. Schweier

Graduate Students:

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C. A. Creutz
H. Diaz
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R. G. Gaunder
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M. V. Olson
J. D. White
A. W. Zanella

Agency Support:

AT (04-3)326, P.A. 6-Mod. 5
NIH GM 13638-02
NSF GP 5322

Technical Objective:

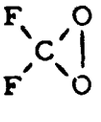
The objective of the work is to reach a fundamental understanding of how one of the two general classes of chemical reactions takes place, namely the class of oxidation-reduction reactions. Most of our current concern is with homogeneous reactions in solution; this choice of area is dictated by the fact that the basic principles governing the mechanisms of reaction have still to be developed, and are more easily traceable in homogeneous systems. One goal of the research is to understand heterogeneous reactions in the same depth, and the program will eventually embrace reactions in which metals are deposited from solutions of their salts, or are converted from the elementary state to salts in solution, whether the changes are brought about by chemical agents or by electrolytic means. A connection between "electron transfer" in the systems we are studying and in solid semiconductors is developing, and the two fields have in common a concern with the mechanism of electron transfer.

Approach:

Any systems chosen for particular study are selected as they qualify in affording opportunities to answer some general question on the mechanism of oxidation reduction reactions. The experiments often call for the preparation of new substances, but the most generally important experimental evidence concerns the identification of intermediate and final products, and the measurement of reaction rates. Modern physicochemical methods such as mass, infrared, nmr, and esr spectroscopy are essential to the progress of the work.

Research Report:

1. Reactions of Metastable Atoms-Matrix Isolation Studies.

Earlier work showed that $O(^1D)$ adds to CO_2 forming CO_3. To explore the generality of the addition of $O(^1D)$ to the carbon-oxygen double bond, we are studying the reaction of $O(^1D)$ with COF_2. A new species is in fact formed when O_3 in a solid COF_2 matrix is illuminated, but we are not yet in position to decide whether it is the expected product  .

The exchange reaction of $S(^1D)$ with CS_2 is being explored. An attempt will be made to learn whether the species CS_3, analogous to CO_3, is formed.

2. Electron Transfer Reactions.

(a) Characterization of reactants.

The chemistry of species of the type $(NH_3)_5Ru^{II}L$ and $(NH_3)_5Ru^{III}L$ is largely unexplored and a study of the substitution and other properties is a necessary prelude to investigating the

electron transfer reactions of the species. The ions of the class $(NH_3)_5Ru^{II}N$⟨⟩R have proven to be especially interesting. They show a strong "charge-transfer" transition in the visible region of the spectrum. The position of the band is sensitive to the nature of R and to changes in the medium.

Current theories of the bonding of the metal to the ligand suggest than an important component of the bond may arise from d electrons of the metal being donated to unoccupied orbitals of the ligand. We have found direct support for this supposition in comparing the acidities of

$(NH_3)_5RuN$⟨⟩NH^{3+}

(I)

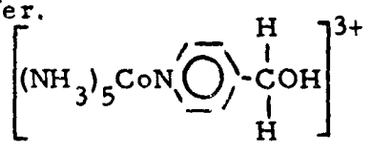
and N⟨⟩NH^{+} (II). Despite the higher charge on (I), it is a <u>weaker</u> acid than (II) by a factor of ca. 100. We take this to be a reflection of the net transfer of electron density from Ru(II) to the ligand in forming the coordinate bond.

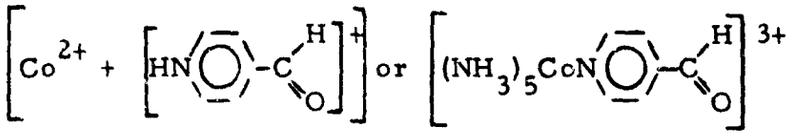
The lability of the coordinated water in $V(H_2O)_6^{2+}$ is important in understanding the oxidation-reduction behavior of this ion. The lability was measured by the line broadening in H_2O^{17} exerted by V^{2+}. Exchange of bound water is remarkably slow in this ion ($k \sim 1.0 \times 10^{2}$ sec^{-1}) and this factor limits the reaction possibilities for this ion when it functions as oxidant.

(b) Comparison of Ru(III) and Co(III) as oxidizing agents.

Differences in the two can be expected because of differences in the symmetry of the acceptor orbitals (this is π for the Ru(III) and σ for Co(III)). One immediate consequence of this difference is that the Ru(II)-L bond in the product is much less substitution-labile than a corresponding Co(II)-L bond. In line with this, numerous Ru(II) intermediates have been encountered in the reduction of Ru(III) complexes (e.g. $\left[(NH_3)_5RuO\overset{H}{C}r\right]^{4+}$, $\left[(NH_3)_5Ru\text{-}O\overset{R}{\underset{}{C}}OCr\right]^{4+}$, $(NH_3)_5RuO_2CR^+$) but none in the reduction of Co(III) complexes. Another consequence of the difference is the fact that the acceptor orbital for Ru(III) overlaps better with the π system of a ligand than does the acceptor orbital for Co(III). We believe that the observation that carboxylate ion is a much more efficient electron mediator in the reduction of Ru(III) than of Co(III) is a manifestation of this.

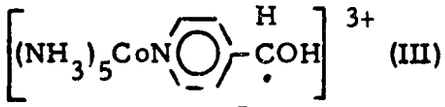
(c) Induced electron transfer.

When a molecule such as  is attacked at the alcohol function by a $1e^-$ oxidant,



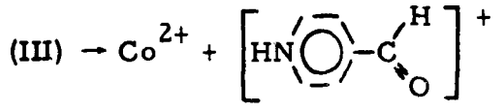
is produced. When a $2e^-$ oxidant is used only the latter product is obtained. The chemistry in the former case comes about because

the radical intermediate

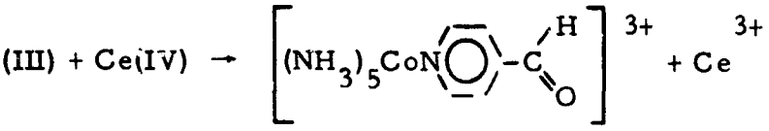


(III)

formed by the attack of the $1e^-$ oxidant decays by internal electron transfer



or by being further oxidized by external oxidant



We have in these systems a probe into the mechanism of oxidation of different functional groups and the opportunity to learn something definite about the internal electron transfer process.

3. The Chemistry of Molecular Nitrogen.

Molecular nitrogen has always been considered to be remarkably inert. Allen and Senoff at the University of Toronto made an important advance in preparing $(NH_3)_5RuN_2^{2+}$ (IV). Other complexes of molecular N_2 have since been prepared. The contribution made here recently was in showing that (IV) is formed by the spontaneous reaction of N_2 with $(NH_3)_5RuOH_2^{2+}$ in aqueous solution at room temperature and furtner in showing that the reaction continues into a second stage

$$(NH_3)_5RuN_2^{2+} + (NH_3)_5RuOH_2^{2+} = \left[(NH_3)_5RuN_2(NH_3)_5\right]^{4+} + H_2O.$$

A compound containing the novel binuclear complex has been prepared and Professor P. Simpson is determining its crystal structure.

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42. STRAIN HARDENING AND FRACTURE OF ALLOYS AND COMPOSITE MATERIALS

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Professional Associate: T. R. Wilshaw

Graduate Students:

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T-W. Chou
F. A. I. Darwish
D. F. DeSante
D. O. Harris
D. E. Hodgson
L. E. Kaechele
C. A. Rau, Jr.
J. L. Watters
A. J. West
R. A. Wullaert

Agency Support:

NASA NsG-622
Army DA-31-124-ARO(D)251
ARPA SD-87
NSF GK 1092 (With Professor C. R. Barrett)

Research Report:

(1) A Theoretical Investigation of Dislocation Distributions in Two-Phase Systems

Graduate Student: D. M. Barnett

Technical Objective:

To determine the stress distributions due to the interaction of various dislocation pile-ups with rigid and finite rigid second phase particles of varying dimensions.

Approach:

Using the method of continuously distributed dislocations, exact analytical solutions were obtained for the stress fields associated with screw dislocation pile-ups against various second phases.

Research Report:

The results obtained were used to discuss relaxation of the pile-up stresses by fracture initiation in the second phase by cross-slip of the leading array dislocations around the second phase.

(2) Elastic Plastic Cracks in Two-Phase Materials

Graduate Student: T-W. Chou

Technical Objective:

Theoretical analysis of crack formation and propagation in fibre composite materials.

Approach:

Theoretical calculations based upon the dislocation distribution approach of Cottrell, Bilby and Swinden, taking into account the rigidity and geometry of the hard phase.

Research Report:

Calculations of plastic zones for various crack distributions in a material with a rigid second phase have been performed. These will be extended to treat materials with second phases of finite rigidity. In addition, an approach based upon classical continuum elasticity will be attempted.

(3) Fracture Mechanisms in Quenched and Temperature Steels

Graduate Student: D. E. Hodgson

Technical Objective:

To determine the mechanism of fracture in a dispersed two-phase system using quenched and tempered steels as a model.

Approach:

Mechanical tests, tensile and slow notched bend, to determine fracture and deformation behavior. Correlation with metallographic and electron fractographic observations.

Research Report:

Experimental work has been almost completed and sufficient data has been obtained for a detailed comparison with existing theories. The validity of the theoretical model will be tested.

(4) Strength and Fracture of Fibre Eutectic Composites

Graduate Student: F. A. I. Darwish

Technical Objective:

To determine the mechanisms of deformation and fracture in a unidirectionally solidified Al-Ni eutectic alloy.

Approach:

Tensile and notch bend tests over a range of temperature. Correlation with metallographic observations and partial loading studies.

Research Report:

Tensile tests revealed a fairly strong temperature dependence of both the fracture stress and tensile elongation. Currently the tensile and notch bend properties are being evaluated as a function of both temperature and strain-rate for three orientations.

(5) Effect of Drilled Holes on Notch Toughness

Graduate Student: C. A. Rau, Jr.

Technical Objective:

To determine the effect of drilled holes on the redistribution of stress around a notch and resulting effects on fracture toughness.

Approach:

Experimental stress analysis using photoelasticity and dislocation etch pit techniques. Fracture measurements using slow-bend and instrumented Charpy tests.

Research Report:

The holes redistributed the plastic strains and reduced the degree

of triaxiality ahead of the notch. The net effect was a reduction of the Charpy impact transition temperature by as much as 60°C.

(6) Fracture of Armor Plate Materials

Research Associate: T. R. Wilshaw

Technical Objective:

To determine the transient stress and strain distributions in a circular clamped plate due to stress pulses and projectiles and to establish a fracture criterion

Approach:

Experimental measurements using a modified version of a Hopkinson bar, dynamic stress measurement using strain gages, visco-plastic stress analysis, fracture observations, final plate deflection.

Research Report:

The theoretical stress distributions (elastic and plastic), and the prediction of final plate deflection are in agreement with experimental measurements, for the highly strain-rate-sensitive materials used.

(7) Microcrack Formation in Polycrystalline Iron

Graduate Student: L. E. Kaechele

Technical Objective:

To determine the relationships between the formation of cleavage microcracks and microscopic stresses and strains, by means of statistical techniques.

Approach:

Tensile testing, microscopic observations of microcrack density and orientations, comparison with theoretical prediction.

Research Report:

The character of the trace angle distributions and a statistical analysis of the data led to the formulation of a stress power model in

which the number of cracks formed at a specific crack plane angle is proportional to a large (eighth to tenth) power of the normal stress across that plane.

(8) Effects of External Loadings on Crack Propagation

Graduate Student: D. O. Harris

Technical Objective:

To investigate the arrest of running cracks below a laterally compressed zone in a plate.

Approach:

Preliminary work is involved in determining the stress distribution in an uncracked plate subjected to opposed lateral compression forces. The stresses in the cracked plate - in the vicinity of the crack tip - will then be deduced approximately from the uncracked stress distribution, in order to assess the possibility of arresting a running crack. A simultaneous related experimental program is being conducted.

Research Report:

The tangential stress in a thick plate subjected to oppositely applied concentrated forces has been determined. This work will shortly be extended to the case in which the load is distributed over a finite circular area. Construction of apparatus for the experimental portion of this investigation is presently underway.

(9) Fracture Toughness and Alloy Development

Graduate Student: R. A. Wullaert

Technical Objective:

To determine the effect of nickel on the fracture toughness of low carbon ferritic steels.

Approach:

The effect of nickel on the important fracture parameters was

determined by use of tensile, slow-bend, and instrumented Charpy tests. The effects of nickel on fracture behavior were divided into microstructural effects and direct or intrinsic effects.

Research Report:

Nickel was found to increase fracture toughness by microstructural changes (refining the grain size and removing grain boundary carbides) and by raising the fracture stress and lowering the temperature, strain rate, and grain size dependence of the yield stress.

(10) Healing of Microcracks by High Temperature Annealing

Graduate Student: D. F. DeSante

Technical Objective:

The purpose of this investigation is to determine whether hydrogen-induced microcracks in iron--3% silicon can be healed by means of high temperature annealing treatments.

Approach:

Microcracks are introduced into tensile specimens of iron--3% silicon by the cathodic charging of hydrogen. These tensile specimens are annealed for times of up to 36 hours at temperatures where recovery and/or recrystallization takes place, and then tested at temperatures between -196°C and 25°C to determine the effectiveness of the healing treatments.

Research Report:

An increase in the microscopic fracture stress, an increase in the total reduction in area at fracture and a lowering of the ductile-brittle fracture transition temperature are found to accompany the annealing of precracked specimens. These effects are believed to result from an increase in the critical plastic strain necessary to initiate fracture, and increase in the tip radii of curvature of the microcracks or both as a result of the annealing treatments. Certain small microcracks are observed to heal completely (disappear) as a result of the

annealing treatments.

(11) Effect of Pre-twinning on the Fracture Toughness of Mild Steel

Graduate Student: J. L. Watters

Technical Objective:

To determine the effects of twinning on the fracture toughness and transition temperature in mild steel as a function of twin density.

Approach:

Shock loading of plates of C-1009 steel to various levels of impulse and peak pressure using sheet explosives.

Determination of effects in impact and slow bend using Charpy specimens cut from the above plates.

Research Report:

Shock loading of plates and machining of specimens has been completed, and testing is now in progress.

(12) Strength of Brazed Joints (With Professor C. R. Barrett)

Graduate Student: A. J. West, Jr.

Technical Objective:

To determine the effect of base metal yield strength and the joint thickness to diameter (T/D) ratio on the joint strength.

Approach:

Drill rod brazed with 99.99% silver under specified conditions of atmosphere and cooling rate. Tensile tests made on joints -- metallographic and fractographic observations.

Research Report:

Joint strengths four to five times the ultimate strength of silver were observed. Specimens of constant base metal yield strength showed

increasing fracture strength as T/D decreased; whereas the macroscopic yield strength remained constant equal to the yield strength of the drill rod.

Reference Publications:

1. D. M. Barnett and A. S. Tetelman, "The Stresses Produced by a Screw Dislocation Pileup at a Circular Inclusion of Finite Rigidity," Canadian J. of Phys. 45, 841-863 (1967).

2. D. M. Barnett and A. S. Tetelman, "The Stress Distribution Produced by Screw Dislocation Pile-ups at Rigid Circular Cylindrical Inclusions," J. Mech. Phys. Solids 14, 329-348 (1966).

3. A. S. Tetelman and C. A. Rau, Jr., "The Effect of Small Drilled Holes of the Notch Toughness of Iron Base Alloys," Proc. The First International Conference on Fracture 12 691-709 (1965).

4. A. S. Tetelman, T. R. Wilshaw, and C. A. Rau, Jr., "The Critical Tensile Stress Criterion for Cleavage," to be published in Proceedings of International Symposium on Fracture Mechanics, Kiruna, Sweden, 1967.

43. DEPENDENCE OF REMANENT MAGNETIZATION ON INTERNAL STRESS IN ROCK-FORMING FERRIMAGNETIC MINERALS

G. A. Thompson, Professor, Geophysics

Graduate Student: Peter N. Shive

Agency Support: NSF GP 5422

Objectives:

To determine the effect of internal stress on the stability of thermoremanent magnetization (TRM) in rock-forming ferrimagnetic minerals, and to test existing theories about the origin of TRM.

Approach:

Determination of magnetostriction and magnetocrystalline anisotropy constants of magnetite from room temperature to the Curie point. Determination of partial TRM characteristics over the same temperature range. Study of the characteristics of TRM acquisition in samples with varying dislocation densities. Development of techniques for direct observation of dislocations and domains in strained samples.

Research Report:

A pilot program to study similar relationships in nickel has been undertaken. Nickel discs, strained by cold rolling,, were allowed to acquire TRM in various external magnetic fields. The intensity of TRM was shown to be directly related to the amount of strain. Anisotropy of TRM observed in most samples is possibly caused by preferential orientation of dislocations.

44. CRYSTALLOGENICS

W. A. Tiller, Professor, Materials Science

Research Associates:

S. O'Hara
W. Oldfield

Graduate Students:

L. F. Donaghey
G. T. Geering
R. Gomez-Ramirez
R. Hiskes
B. K. Jindal
H.-S. Kim
G. R. Kotler
M. V. Rao
T. Surek
T. Takahashi
L. A. Tarshis

Agency Support:

AFOSR-731-65
ARPA SD-87

Technical Objective:

To gain a complete and quantitative understanding of the crystallization process by controlling the state of chemical and physical perfection of crystals through control of the freezing process. The ultimate aim is the optimization and control of certain material properties.

Approach:

Theoretical and experimental investigations of all the important elements of the crystallization process: nucleation, interface attachment kinetics, solute transport, fluid motion, interface morphology, physical imperfections and phase equilibria. The experiments are being carried out on a broad range of materials to elucidate the essential physics of the problems.

(1) Consequences of Free Electron Equilibrium on Interface Characteristics

Graduate Students: B. K. Jindal
T. Takahashi

The requirement of electronic equilibrium being attained at interfaces leads to the formation of space charge layers in any two phases involved in a transformation reaction. The thickness of the layers is sufficient, even in metallic systems, to cause adsorption of very polarizable ions (atoms) to the interface region. This adsorption affects the surface energy, layer motion kinetics and solute partitioning during freezing. These effects are being investigated in the ice-water system and in low-melting metallic systems.

The satisfaction of electronic equilibrium at the interface between a substrate and a pure liquid or pure solid requires the transfer of charge from one phase to the other. The energy change associated with this charge transfer is significant for certain systems and favors the presence of solid in contact with the substrate. Such systems make good nucleation catalysts. This study is a theoretical investigation of the important material parameters involved in the electrostatic aspects of heterogeneous nucleation for both pure and alloy melts and includes experimental investigations of the nucleation of low melting metals by single crystal silicon substrates.

(2) Non-Equilibrium Interface Kinetics

Graduate Student: R. Hiskes

The effect of transformation velocity on the incorporation of non-equilibrium solute content is being investigated for the domain of high transformation rates, i.e., a solute content not consistent with phase diagram partitioning and conventional transport analysis. The theoretical study involves (i) the analysis of phase diagrams to determine the electrochemical potential of the major and minor constituents as a function of concentration and temperature, (ii) the statistical mechanical determination of the interface transfer processes and (iii) the solution of the crystal boundary-value problem for heat transport, matter transport, attachment processes and capillarity effects. The experimental study involves the use of germanium as a substrate with different low-melting metals as the solutes.

(3) Interface Morphology

Graduate Students: L. F. Donaghey
G. T. Geering
G. R. Kotler
L. A. Tarshis

A theoretical and experimental study of dendritic growth has been undertaken. A perturbation analysis of dendrite side-branch formation for a pure system as a function of the interface attachment kinetics has been carried out for simple attachment kinetics. It showed that the optimum side-branch spacing depended sensitively on the magnitude of the attachment resistance. A steady-state analysis of the growth of a non-iosthermal and non-isoconcentrate dendrite tip has revealed that the tip velocity is a sensitive function of alloy content and that at low alloy content, the tip velocity increases with increase of alloy content, whereas, at high alloy content, the tip velocity decreases with increase of alloy content. On the experimental side, a new dendrite orientation has been observed in tin which can be understood only by the theory of non-isothermal dendrite-tip growth.

The dendrite morphology is normally thought of as a particular crystal morphology with well-defined crystallographic features and is normally associated with metals or other simple solids. On the other hand, the spherulite is normally thought of as a crystal morphology, unique to polymeric systems or complex solids, which exhibits non-crystallographic features. Ice crystallized from certain aqueous solutions is found to undergo a transition from the one crystal morphology to the other as the crystallization conditions are varied. Investigation in this area is directed at a detailed understanding of why this transition occurs and if it is a general phenomenon.

A theoretical investigation of the stability of a planar interface during crystallization in various thermal and solute fields as a function of the operative attachment kinetic mechanism has been carried out. It has been shown that, for the uniform attachment mechanism and for layer edge-limiting attachment mechanisms, the effect upon the onset of cell formation is negligible. However, for layer source-limiting attachment

mechanisms, the effect upon the onset of cell formation may be extremely large and may stabilize a planar interface in the presence of a large degree of constitutional supercooling.

The stability and morphology analyses have been extended to the treatment of two-phase co-operative eutectic growth where the aggregate may be either lamellar or rod-like in nature.

(4) Controlled Fluid Motion

Graduate Students: H. Kim
W. Oldfield
M. V. Rao

Much of the work in this area is concerned with the application and utilization of fluid motion which is generated and controlled largely by the application of moving electromagnetic fields. One study concerns the investigation of the important factors involved in large volume purification systems utilizing controlled freezing. Another concerns the determination of the distribution coefficients of all constituents in multicomponent technical alloys. A third concerns the investigation of the important process variables and materials parameters controlling the crystal multiplication produced by the segmentation of dendrites. The crystal multiplication considerations teach one the path to generating a new foundry technology which uses controlled fluid motion during freezing to produce fine-grained homogeneous ingots and castings of a wide variety of materials.

(5) Growth and Perfection of Crystals

A high temperature (1000°C - 3000°C) chamber and control system have been developed for the Czochralski growth of crystals in this melting point range. Techniques have been developed for the growth of single crystals of sapphire and ruby. The perfection of these crystals may be altered by changes in the environmental conditions and are being evaluated by using metallographic, optical and X-ray topographic techniques.

(6) Industrial Application Areas

The fundamental understanding and the crystallization technology generated by the foregoing studies will find ready application in the following industries: (i) single crystals, (ii) chemical purification, (iii) ingots and castings, (iv) chemical crystallizers, and (v) frozen foods.

Reference Publications:

1. B. K. Jindal and W. A. Tiller, "On Electrostatic Potentials at the Ice-Water Interface," accepted for Publication, Surface Science (Dec. 1967).

2. S. O'Hara and W. A. Tiller, "The Effect of Fluid Motion on the Grain Size of Tin," Trans. AIME 239, 497 (1967).

3. L. A. Tarshis and S. O'Hara, "A Method for Determining Molecular Attachment Kinetics During Crystal Growth, I. Theory," J. Appl. Phys. 38, 2086 (1967).

4. L. A. Tarshis and G. R. Kotler, "Comments and Criticisms of the Paper "Investigation of the Solid/Liquid Interface Temperature Via Isenthalpic Solidification'," accepted for publication in I.J.C.G (Dec. 1967).

5. S. O'Hara, L. A. Tarshis, and W. A. Tiller, "Limitations of the Thermal Wave Technique for Determining Molecular Attachment Kinetics," J. Chem. Phys. 46, 2800 (1967).

6. S. O'Hara, "Web-Dendrite Growth of Single Crystals of Tin," I.J.C.G. 1, 73 (1967).

7. W. Oldfield, G. T. Geering, and W. A. Tiller, "The Evolution of Crystal Shape: A Computer Model," Materials Science and Engineering (July 1967).

8. W. A. Tiller, "The Generation of Science-Based Technology in the Field of Crystallization," Proceedings of the O.A. R. Research Applications Conference, p. 109, Washington, D. C. (Mar. 1967).

45. PHASE RELATIONSHIPS IN MINERAL SYSTEMS

O. F. Tuttle, Professor, Geology

Graduate Students:

J. H. Carman
G. E. Lofgren
R. F. Martin
J. R. Weidner

Agency Support:

NSF GA 474
NSF GA 653

Research Report:

(1) Phase Relationships

Graduate Students: J. H. Carman
R. F. Martin
J. R. Weidner

Technical Objective:

The determination of the formation, thermal stability and phase relationships in synthetic chemical systems which simulate portions of natural rock forming systems, their minerals and processes in the crust of the Earth.

Approach:

Small charges enclosed in gold, platinum or silver palladium were held at temperature (400 to 1200°C) and pressure (250 to 10,000 bars) for hours to weeks then quenched and examined for their phase content. This technique was supplemented by differential thermal analysis in a similar PT range.

The system $NaAlSiO_4$-Mg_2SiO_4-SiO_2-H_2O (J. H. Carman)

The phase relationships between nepheline, sodium phlogopite, forsterite, albite, enstatite, β quartz, spinel ($MgAl_2O_4$), liquid and

vapor have been determined and shown to be quaternary over a large range of temperature and pressure. The relations obtained have a bearing on the understanding of the chemistry of basalts and more siliceous igneous rocks and their metamorphic equivalents.

One phase sodium phlogopite was described for the first time. The high thermal stability of this 10 Å mica, $NaMg_3AlSi_3O_{10}(OH)_2$, was determined and in addition it was found to form two new hydrates at lower temperature containing two and four moles of H_2O per formula weight respectively. This montmorillonite-like behavior at low temperatures combined with high thermal stability make sodium phlogopite somewhat unique in the field miceaous material. The relative instability of Na^+ in the interlayer position in the 12 Å hydrate or in the 15 Å hydrate probably accounts for its absence in natural rocks but the nature of the natural exchange process is not known.

The system $Na_2Si_2O_5$-$NaAlSi_3O_8$-SiO_2- H_2O (J. H. Carman)

The relations in the quaternary system are controlled to a great extent by the presence of $Na_2Si_2O_5$ which lowers the temperature for the coexistence of albite + quartz + liquid and by the relations along the $Na_2Si_2O_5$-H_2O join which contains critical (Liquid = Vapor) relations at low temperatures.

From the materials point of view this system and its subsystem, (e.g., $Na_2Si_2O_5$-SiO_2-H_2O) offers a simple and efficient model for hydrothermal crystal growth systems because of the solubility of SiO_2 is increased significantly in $Na_2Si_2O_5$-rich aqueous vapor and liquid.

The system Fe-C-O (J. R. Weidner)

The univariant reactions hematite + siderite = magnetite + vapor and siderite = magnetite + graphite + vapor were determined in the low temperature sub-solidus region. A discontinuity in the siderite stability curve suggests the possibility of a high pressure, non-quenchable polymorph of $FeCO_3$; perhaps analogous to Calcite II.

Additional relations include ten univariant reactions and three invariant points involving γ iron, wustite, magnetite, graphite, oxide liquid, metallic liquid, and vapor were determined. The oxide liquid was first encountered at 815°C and 350 bars and the metallic was first encountered at 875°C and 500 bars. The two liquids coexist at 1142°C from low to high pressures.

These data contribute fundamental information bearing on the origin and processing of iron.

The Systematic Study of Feldspars (R. F. Martin)

Feldspars, characterized by the general formula $X(Al,Si)_4O_8$, where X may be Na, K or Ca, constitute a major fraction of the earth's crust. Current research on this most important and complex family of minerals include the following:

1. synthesis of the ordered (i.e., Si-Al distribution) polymorph of albite, $NaAlSi_3O_8$, and orthoclase K Al Si_3O_8.
2. synthesis of non-stoichiometric albites; the effect of these departures from stoichiometry on lattice parameters and stability.
3. study of reactions that found the lower thermal stability field of albite as a function of pressure and temperature.

(2) The Devitrification of Natural Glass

Graduate Student: G. E. Lofgren

Technical Objective:

To study the devitrification process in natural glass and to clearly distinguish the textures which reflect that such a process has taken place.

Approach:

Natural glass cores were enclosed in gold capsules containing various solutions from distilled water to highly alkaline solutions;

with or without chloride ion. These charges were held at temperature (20° to 700°C) and pressure (1 to 4,000 bars) for variable lengths of time and then rapidly cooled, and examined.

Research Report:

Results show that the presence of Na^+ or K^+ in the fluid during devitrification increases the rate of devitrification. The rate of devitrification is a function of alkali concentration and temperature.

These studies help elucidate the structure of natural glasses, and the devitrification process in the presence of alkaline environments. The spherulitic dendrites which commonly result from low temperature devitrification appear to have natural analogs suggesting the application of this study to natural rocks.

46. FUNDAMENTAL STUDIES OF MAGNETIC MATERIALS

R. L. White, Professor, Electrical Engineering and Materials Science

Professional Associate:

T. G. Phillips

Graduate Students:

J. W. Allen
T. J. Beaulieu
R. W. Bené
Y. Satoda
R. L. Townsend, Jr.

Agency Support:

ONR Nonr 224(83)
NSF GK 202
ARPA SD-87

Technical Objective:

To understand the macroscopic properties of magnetic materials in terms of the atomic properties of the constituents.

Approach:

Spectroscopic studies, principally electron paramagnetic resonance and optical absorption, are conducted on the relevant magnetic ions, and the results of these studies are correlated with the macroscopic magnetic properties of solids built of these atoms.

Research Report:

The research effort consists of several interrelated studies. I shall fairly arbitrarily separate these projects into Studies of Magneto-elastic Effects, Studies of the Rare Earth Orthoferrites, and Studies of Exchange.

A. Studies of Magnetoelastic Effects

We have conducted a series of experiments with very gratifying results directed at understanding magnetoelastic effects in magnetic insulators on an atomic basis. We make what is called a single-ion model of the magnetic material, in which we regard the crystal as being an assembly of elementary atomic magnets coupled by an exchange interaction. Such a model seems to work well for magnetic insulators but not for magnetic metals, where an itinerant-electron band-model must be used. The single-ion model has been used to predict correctly such properties as saturation moment or magnetic anisotropy but not previously for the somewhat more subtle magnetoelastic properties.

The two most important magnetoelastic effects are magnetostriction and piezomagnetism. The former, which is by far the better known and more important technologically, describes the change in dimensions of a ferromagnetic body as the direction of magnetization is altered. Magnetostriction is quadratic in the magnetization coordinates, that is, reversing the magnetization direction leaves the distortions unchanged (rotation through smaller angles does not). Piezomagnetism is characteristic primarily of antiferromagnets and is linear in the magnetization coordinates—reversing the direction of the net magnetization changes a contraction into an expansion. All magnetoelastic effects have their origin in the strain dependence of magnetic anisotropy, in the fact that distorting the crystal will change somewhat the "easy" direction of magnetization in the crystal. Magnetic materials have an easy direction of magnetization because some directions of the individual atomic moments produce lower energies for the atomic states involved. The atoms have discrete energy levels which may be described by quantum mechanics. Our experiments have been essentially to observe these energy levels by spectroscopic means and then to observe further whether the lowest levels are raised or lowered when we squeeze on the crystal in certain directions. All systems seek their lowest energy state. If squeezing on a crystal lowers the lowest energy states, then a contraction in the same direction is energetically favorable and will occur spontaneously. If we can

measure quantitatively the amount of energy lowering per unit distortion we can predict quantitatively the spontaneous distortions to be expected for the magnetized crystals--the magnetoelastic constants of the crystal.

We have applied this concept with considerable success to a series of compounds. We have observed the variation with strain of the EPR spectrum of a number of ions in the garnet structure and from this data predicted correctly the sign and approximate magnitude of the magnetostriction constants of several rare earth garnets. We have interpreted the strain dependence of the EPR spectra of several transition metal ions in MgO to predict correctly the magnetostriction of various transition metal monoxides (NiO, FeO, CoO, MnO). We have studied the strain dependence of the EPR spectrum of Fe^{3+} in Al_2O_3 and predicted the piezomagnetic constants of αFe_2O_3, and we have measured the strain dependence of Co^{2+} in ZnF_2 to obtain the piezomagnetic constants of CoF_2. We have developed the atomic theory of magnetostriction and piezomagnetism so that we can now predict the temperature dependence of these properties. One result of our studies is to predict the existence of piezomagnetism in a number of compounds in which it has never been observed, so we are now constucting apparatus to study the piezomagnetism in these compounds.

B. Studies of the Rare Earth Orthoferrites

The rare earth orthoferrites are a family of oxides displaying very interesting magnetic behavior. Their chemical formula is $RFeO_3$, where R is a rare earth ion. The iron ions are strongly exchange coupled and order at a relatively high temperature, approximately 650°K. The rare earth ions order quasi-paramagnetically in the exchange field generated by the ordered iron ions. Some of the interesting features of this system are (1) the iron ions form a canted antiferromagnetic array, indicating the presence of antisymmetric exchange between iron ions; (2) the rare earth ions polarize with a net moment essentially perpendicular to the iron spins. The exchange between the iron ions and the rare earth ions must be anisotropic or perhaps anisymmetric; (3) there are several spin configurations compatible with the crystal structure;

all of these spin configurations are found in the rare earth orthoferrite family, and most members of the family assume at least two different allowed configurations at different temperatures. We have been conducting studies to understand the nature of the exchange interactions in these materials and to understand the cause of the spin configuration changes.

There have been two major facets to this program so far. One of these involved the study of the GdFe exchange in $GdFeO_3$ by studying the EPR spectra of Gd^{3+} in $LuFeO_3$. The Gd^{3+} and Fe^{3+} ions are both isotropic S-states, so we expected this interaction to be nearly isotropic. Exchange with the Fe-lattice affects the EPR spectrum greatly, but we were able to analyze this data to establish an isotropic Gd-Fe exchange on the same order as the Gd-Fe exchange in garnets. Our second study involved measuring the spontaneous moment of $YbFeO_3$ at various low temperatures above and below its spin flip temperature (8°K). Though the data raises nearly as many questions as it answers we have established clearly that the off-diagonal elements of the R-Fe exchange tensor are responsible for the polarization of the rare earths. These elements describe either anisotropic but symmetric exchange (which tends to set spins parallel) or anisymmetric exchange (which tends to set spins at right angles). Though the evidence is not complete, anisotropic but symmetric exchange appears to be the correct source. We are inaugurating optical studies of the exchange splittings to see if we can obtain more direct information on these interactions.

C. Studies of Exchange

Under this title we will report optical studies of the Cr^{3+} - Cr^{3+} exchange in Cr_2O_3, and EPR and NMR studies of the Cr^{3+} - Cr^{3+} exchange in $CrBr_3$, $CrCl_3$, and CrI_3. Cr_2O_3 is isostructural with Al_2C_3 or ruby. The Cr^{3+} ions show an energy level structure in Cr_2O_3 similar to what they display in ruby, but modified importantly by the exchange interaction. We have been studying the transition which corresponds to the "R" lines in ruby. One can understand some of the qualitative features of the Cr^{3+} spectrum in Cr_2O_3 on a single-ion basis -- by comparison with

the spectrum of Cr^{3+} dilutely incorporated into Al_2O_3 -- but many important features of the spectrum cannot be so understood. There are important energy level degeneracies which arise from the fact that there are four magnetic ions per unit cell. Group theory can tell us about the number and nature of these degeneracies, and the optical studies in the presence of an applied magnetic field or strains can evaluate the magnetic parameters involved. Such studies are under way, and much of the many-body theory necessary to interpret the spectra has now been developed.

The chromium tri-halides are a family of layer-type compounds which have hexagonal layers of strongly coupled Cr^{3+} ions, with weaker magnetic coupling between layers. The interlayer coupling is sometimes ferromagnetic ($CrBr_3$) and sometimes antiferromagnetic ($CrCl_3$). We wish to study the interlayer exchange by (a) monitoring the Neel temperature of the compound (by NMR) as the interlayer distance is changed by squeezing (b) observing the Cr^{3+} - Cr^{3+} exchange by observing the EPR spectra of Cr^{3+} - Cr^{3+} coupled pairs. Because of large magneto-elastic losses in the samples, near the Neel temperature we find that the EPR results are by far the more promising. We have spectra embarassingly rich in absorption lines and are now sorting these transitions out in order to interpret them. It appears that there are both ferromagnetic and antiferromagnetic interlayer pairs, and the cancellation effects between them lead to the small net interlayer exchange.

Reference Publications:

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2. R. L. White, T. G. Phillips, and R. A. Lefever, "Paramagnetic Resonance Spectrum of Ce^{3+} in Yttrium Gallium Garnet," J. Appl. Phys. Comm. 38 (1) 408-409 (Jan. 1967).

3. T. G. Phillips and R. L. White, "EPR Pressure Experiments on Rare Earths in Diamagnetic Garnets and the Single-Ion Magnetostriction of Rare-Earth Iron Garnets," J. Appl. Phys. 38 (3) 1222-1223 (Mar. 1967).

4. T. G. Phillips, R. L. Townsend, Jr., and R. L. White, "Piezomagnetism of CoF_2 and αFe_2O_3 from EPR Pressure Experiments," Phys. Rev. Lett. 18 (10) 646-647 (Apr. 1967).

5. T. J. Beaulieu, "Temperature Dependence and Anisotropy of Magnetization of Ytterbium Orthoferrite," Microwave Laboratory Report No. ML 1530, Stanford University (Apr. 1967).

6. T. G. Phillips and R. L. White, "Microscopic and Macroscopic Magnetoelastic Tensors for the Rare Earth Garnets from Electron Paramagnetic Resonance under Pressure," Phys. Rev. 160 92) 316-327 (Aug. 1967).

47. SOLID STATE THEORY

R. M. White, Assistant Professor, Physics

Graduate Student:

C. M. Hogan

Agency Support:

ARPA SD-87

Technical Objective:

To develop a microscopic understanding of various magnetic phenomena including optical absorption in antiferromagnets, the nature of impurity modes in ferromagnets, the origin of antisymmetric exchange in garnets, and the behavior of ferromagnetic semiconductors.

Approach:

Our approach to these problems is to develop a model which may be used as a basis for theoretical calculations.

Progress:

We have investigated the indirect magnetic coupling between two impurity spins imbedded in a ferromagnetic linear chain Using a Green's function technique we obtained an exact solution to this problem which revealed that this coupling is much stronger than would be predicted by a spin wave scattering theory. We believe this to be the dominant mechanism for broadening the local mode absorption spectrum.

Reference Publications:

1. D. D. Sell, R. L. Greene, and R. M. White, "Optical Exciton-Magnon Absorption in MnF_2," Phys. Rev. 158 (2) 489-510 (June 1967).

2. R. M. White and C. M. Hogan, "Coupling Between Impurity Spins in a Magnetic Host," submitted to Phys. Rev.

48. MECHANICAL PROPERTIES OF NATURAL MINERALS AND COMPOSITE STRUCTURES

C. Young, III, Assistant Professor, Geophysics

Graduate Student:

B. R. Clark

Agency Support:

USDI #14-08-0001-10525
NSF GA 671 (with Professor B. M. Page, Geology)
ARPA SD-87

Research Report:

(1) Dislocations in the Deformation of Ultra-Mafic Minerals

Technical Objectives:

To determine the role of dislocations in the deformation of olivine, $(Mg, Fe)_2 SiO_4$, and other ultra-mafic minerals under varying conditions of high pressure and temperature.

Approach:

Development of techniques for directly observing dislocations in ultra-mafic minerals. Determination of the dependence of dislocation densities and velocities upon stress, strain and strain history. Development of mathematical models for integrating observed dislocation behavior into the large scale behavior of massive ultra-mafic bodies with particular emphasis on the origin of deep earthquakes. Investigation of the relationships between single crystal dislocation phenomena and the mechanical behavior of polycrystalline bodies.

Progress:

During previous periods techniques for directly observing dislocations in olivine were developed and the important dislocation parameters (density vs. strain and velocity vs. stress) were determined for the important [001] - {110} slip system in single crystal deformation.

Further application of these data to models for large scale inhomogeneous deformation has demonstrated the very important roles that dislocation depinning and multiplication rates could play in ductile earthquake mechanisms. An experimental program involving the triaxial deformation of polycrystalline olivine samples at pressures up to 10 kilobars and temperatures up to 1000°C has been initiated. The results from these experiments will be used to further extend the single crystal phenomena to polycrystalline deformation.

(2) Influence of Inhomogeneous Deformation upon Fracturing and Shearing of Rocks

Technical Objectives:

To quantitatively describe the fundamental phenomena involved in the fracturing and shearing of monomineralic rocks such that these data may be applied to models for large scale deformation.

Approach:

Development of techniques for etching dislocations, twins and microfractures in calcite, $CaCO_3$. Application of these techniques to the description of fracture controlling phenomena in experimentally deformed polycrystalline samples. Development of basic criteria for fracturing and shearing of polycrystalline $CaCO_3$ bodies. Application of these criteria to models for large scale inhomogeneous deformation such as would occur during seismic rupturing.

Progress:

Chemical etchants which can reveal dislocation, twin and microfracture structures at polished surfaces have been developed. The study of naturally and experimentally deformed polycrystalline $CaCO_3$ samples suggests that fracturing processes are dominantly controlled by twinning. Most significantly, intergranular fractures are formed at the intersection of twins and the stress at fracture tips may be relaxed by twins.

(3) Experimental Development of Preferred Orientations in Clay/Mica Aggregates

With Professor B. M. Page

Technical Objective:

To investigate the mechanical and chemical processes by which preferred orientations are formed in clay and mica aggregates at high temperatures and pressures.

Approach:

Experiments are being developed to simulate the physical environment in which the platy components of rocks in the earth's crust develop strong preferred orientations. The pressure apparatus in which the experiments are conducted permits accurate measurement of confining pressure, temperature, axial load, pore pressure, strain rate, and total strain. Both pure kaolinite ($Al_4Si_4O_{10}(OH)_8$) and montmorillonite ($Al_4Si_8O_{20}(OH)_4 \cdot 8H_2O$) along with powdered natural shales are being studied. The mechanical processes involve the reorientation of inequidimensional grains during the deformation of an initially random fabric. Reduction of intergranular friction by adsorbed water probably plays an important role in such mechanical processes. The chemical processes involve the recrystallization of clays and micas in a non-hydrostatic environment. Particular attention is being devoted to an evaluation of: 1) the effect of adsorbed water upon the mechanical properties of clay aggregates, 2) the validity of several mechanical and chemical processes, and 3) the relative importance of each process in producing preferred orientations. The nature of the preferred orientations produced is measured by optical and X-ray techniques.

Progress:

Mechanical reorientation is affected largely by directional compaction. An anisotropic reduction in volume associated with the removal of pore fluids (H_2O) greatly enhances the degree of preferred orientation. Weak preferred orientations may be developed in clay

samples with as little as 5% water at 200°C and 30,000 psi. after 20% strain. The brittle-ductile transition under the same conditions occurs with a water content of less than 5% for synthetically precompacted clays.

Initial attempts to evaluate the effects of a non-hydrostatic stress state upon crystallization at 500°C and 30,000 psi. have produced little or no change in preferred orientation of muscovite from kaolinite plus potassium ions.

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SECTION D

DOCTORAL DISSERTATIONS

1. D. M. Barnett, "A Theoretical Investigation of Dislocation Distributions in Two-Phase Systems," Materials Science (April 1967)

2. T. J. Beaulieu, "Temperature Dependence and Anisotropy of Magnetization of Ytterbium Orthoferrite," Applied Physics (June 1967)

3. L. J. Berliner, "Spin Label Studies of α-Chymotrypsin," Chemistry (June 1967)

4. G. H. Blount, "Photoelectronic Properties of ZnS Single Crystals with Imperfections Induced by Annealing or by Radioactive Impurities," Electrical Engineering (April 1967)

5. M. G. Buehler, "A Point-Contact Method for Determining the Charge Carrier Density and Mobility in Thin Semiconducting Layers," Electrical Engineering (Sept. 1966)

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7. H. D. Cohen, "Nuclear Magnetic Susceptibility of a Dilute Mixture of He^4 in He^3," Physics (Sept. 1966)

8. E. A. Deutsch, "Studies on the Acetatopentaaquochromium(III) Ion," Chemistry (June 1967)

9. C.-Y. Duh, "Hot Electron Transport in Silicon at High Electric Fields," Electrical Engineering (June 1967)

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11. W. F. Egan, "Microwave Propagation in Periodic Ferrite Structures," Electrical Engineering (June 1967)

12. B. E. Eichinger, "The Thermodynamics of Polymer Solutions," Chemistry (June 1967)

13. N. M. El-Tayeb, "The Diffusion of Hydrogen in Liquid Iron," Mineral Engineering (Sept. 1966)

14. P. L. Guéret, "Wave Propagation and Instabilities in Semiconductors," Electrical Engineering (June 1967)

15. W. H. Haydl, "Current Instabilities in Piezoelectric Semiconductors," Electrical Engineering (April 1967)

16. G. B. Hess, "Measurements of Angular Momentum in Superfluid Helium," Physics (June 1967)

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19. B. G. Huth, "The Stimulated Raman Effect in an Off-Axis Resonator," Electrical Engineering (June 1967)

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23. E. G.-H. Lean, "Studies of Microwave Shear Waves in Solids," Electrical Engineering (June 1967)

24. D. M. Loescher, "A Crystal Field Analysis of Cobalt Impurities in GaP," Electrical Engineering (Jan. 1967)

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53. C. Young III, "Applications of Dislocation Theory to Upper-Mantle Deformation," Geophysics (Sept. 1966)

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N. N. Singh-Deo

A. A. Solomon
R. G. Stang
G. B. Stringfellow
T. Surek
T. Takahashi

L. A. Tarshis
T. A. Taylor
J. L. Watters
A. J. West
R. A. Wullaert

R. R. Zupp

MINERAL ENGINEERING

A. Ahmed
S. Akhtar
R. N. Anderson
R. L. Burns
P. J. Depuydt
M. M. A. El-Naggar

N. M. El-Tayeb
W. H. Goodnow
J. Lee
M. Müller-Henneberg
T. E. Paces
S. D. Peng

E. M. Sacris
I. D. Shah
C-S. Shi
R. W. Smith
M. C. Speer
M. T. Utine
L. R. Velho

PHYSICS

M. J. Berggren
B. L. Beron
T. D. Bracken
R. E. Brown
D. E. Claridge

H. D. Cohen
E. P. Day
J. L. Emmett
D. H. Frieberg
S. H. Gerber

D. B. Greene
R. L. Greene
H. M. Griffiths
R. B. Hallock
A. F. Hebard
G. B. Hess

C. M. Hogan
L. B. Holdeman
J. F. Holzrichter
J. Jehl
S. A. Johnson

L. W. Kunz
C. Lyneis
J. M. Madey
B. McCaul
L. M. Middleman

E. D. Nelson
J. C. Nickerson, III
C. H. Ostfeld
J. L. Rapier
J. M. Pierce
P. B. Pipes

G. E. Possin
D. K. Rose
D. D. Sell
N. P. Shah
K. W. Shepard

S. T. Spence
S. E. Stokowski
L. R. Suelzle
M. Taber
W. B. Tiffany

W. J. Trela
J. P. Turneaure
S-T. Wang
J. P. Webb
E. Wilson
J. Y-M. Wong

OTHER DEPARTMENTS AND DIVISIONS

CIVIL ENGINEERING

W. H. Bray
F. Radjy
E. J. Sellevold

GEOLOGY

J. H. Carman
B. R. Clark
R. D. Lawrence
G. E. Lofgren
R. W. Luce
R. F. Martin

GEOPHYSICS

J. D. Johnson
T. E. Landers
C. F. Peterson
P. N. Shive
R. L. Wesson

ENGINEERING MECHANICS

D. O. Harris
L. E. Kaechele

MECHANICAL ENGINEERING

T. L. Gerber

IV. GRADUATE DEGREES CONFERRED

Doctor of Philosophy

D. M. Barnett	Materials Science
T. J. Beaulieu	Applied Physics
L. J. Berliner	Chemistry
G. H. Blount	Electrical Engineering
M. G. Buehler	Electrical Engineering
D. E. Caddes	Electrical Engineering
H. D. Cohen	Physics
E. A. Deutsch	Chemistry
C.-Y. Duh	Electrical Engineering
R. C. Eden	Electrical Engineering
W. F. Egan	Electrical Engineering
B. E. Eichinger	Chemistry
N. M. El-Tayeb	Mineral Engineering
P. L. Guéret	Electrical Engineering
W. H. Haydl	Electrical Engineering
G. B. Hess	Physics
R. C. Hughes	Chemistry
J. K. Hurst	Chemistry
B. G. Huth	Electrical Engineering
L. E. Kaechele	Engineering Mechanics
W. H. Kleinfelder	Electrical Engineering
W. F. Krolikowski	Electrical Engineering
E. G.-H. Lean	Electrical Engineering
D. H. Loescher	Electrical Engineering
O. P. McDuff	Electrical Engineering
T. J. Meyer	Chemistry
E. D. Nelson	Physics
F. R. Nordmeyer	Chemistry
C. B. Norris, Jr.	Electrical Engineering
R. A. Orwoll	Chemistry
L. M. Osterink	Electrical Engineering
T. J. Paoli	Applied Physics
D. W. Peters	Electrical Engineering
R. J. Powell	Electrical Engineering
H. J. Price	Chemistry

GRADUATE DEGREES CONFERRED

Doctor of Philosophy (Continued)

S. Puri	Electrical Engineering
H. E. Puthoff	Electrical Engineering
C. A. Rau	Materials Science
S. D. Sample	Chemistry
D. D. Sell	Physics
I. D. Shah	Mineral Engineering
N. P. Shah	Physics
J. L. Shay III	Electrical Engineering
K. K. Shih	Electrical Engineering
M. Shyam	Electrical Engineering
H. Sonnenberg	Electrical Engineering
S. T. Spence	Physics
L. R. Suelzle	Physics
D. D. Thusius	Chemistry
W. B. Tiffany	Physics
W. J. Trela	Physics
J. P. Turneaure	Physics
C. Young III	Geophysics
A. Y.-C. Yu	Electrical Engineering
R. R. Zupp	Materials Science

GRADUATE DEGREES CONFERRED

Master of Science

R. L. Beyer	Applied Physics
F. R. Brown III	Chemistry
C. A. Bruce	Chemical Engineering
M. L. Burack	Applied Physics
W. R. Callen, Jr.	Applied Physics
W. D. Callister	Materials Science
D. E. Claridge	Physics
J. R. Costa Guimarães	Materials Science
F. A. I. Darwish	Materials Science
W. N. Delgass	Chemical Engineering
D. F. DeSante	Materials Science
L. F. Donaghey	Materials Science
D. Farrington	Electrical Engineering
A.-P. Fayet	Materials Science
A. M. Gaylord	Materials Science
R. B. Hallock	Physics
Y. E. Imbert	Materials Science
J. D. Johnson	Geophysics
W. R. Johnson	Materials Science
F. G. Larson, Jr.	Materials Science
C.-m. Lee	Chemical Engineering
G. A. Melin	Chemical Engineering
T. V. Nordstrom	Materials Science
M. V. Rao	Materials Science
C. L. Robinette, Jr.	Electrical Engineering
S. L. Robinson	Materials Science
L. P. Solie	Applied Physics
K. Ushiba	Chemical Engineering
M. T. Utine	Mineral Engineering
L. R. Velho	Mineral Engineering
D. C. Wolkerstorfer	Applied Physics
A. B. Walters	Chemical Engineering
M. T. Wauk II	Applied Physics
S. I. Wax	Electrical Engineering
A. J. West	Materials Science
D. A. Wilson	Applied Physics

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